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(54)【発明の名称】　ペロブスカイト型又はペロブスカイト類似型酸化物担持触媒の製造方法

(57)【要約】
【目的】　所望の種々の担体上にペロブスカイト型酸化物又はペロブスカイト類似型酸化物を高分散状態（高表面積）に安定に担持させ、脱硝酸反応、完全酸化反応等の排ガス浄化処理反応をはじめとする各種の触媒反応に対して、優れた触媒活性及び耐久性等を発揮する多種多様な組成及び性状の高性能のペロブスカイト類酸化担持物触媒を容易にしかも安価に製造する方法を提供する。
【構成】　エーテル結合を持つアルコールと窒素含有アルコールからなる溶媒に少なくともペロブスカイト型あるいはペロブスカイト類似型酸化物の形成原料である金属塩及び／又は金属錯体を溶解してなる溶液を担体に含浸し、熱分解するペロブスカイト型又はペロブスカイト類似型酸化物担持触媒の製造方法。

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【特許請求の範囲】

【請求項１】　エーテル結合を持つアルコールと窒素含有アルコールからなる溶媒に少なくともペロブスカイト型あるいはペロブスカイト類似型酸化物の形成原料である金属塩及び／又は金属錯体を溶解してなる溶液を担体に含浸し、熱分解することを特徴とするペロブスカイト型又はペロブスカイト類似型酸化物担持触媒の製造方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、ペロブスカイト型又はペロブスカイト類似型酸化物担持触媒の製造方法に関し、更に詳しく言うと、各種の酸化物系担体上に少なくともペロブスカイト型酸化物及び／又はペロブスカイト類似型酸化物が分散性よくかつ安定に担持されている多種多様な組成及び性状の担持触媒を容易に製造する方法に関する。本発明の方法により得られた触媒は窒素酸化物（NO_x）、ＣＯ、炭化水素（ＨＣ）等の除去触媒、脱水素触媒、水素化分解触媒触媒等として好適に利用することができる。

【０００２】

【従来の技術】ペロブスキー石（$CaTiO_3$）あるいはこれと同様の結晶構造を有し、いわゆる化学式ＡＢＯ$_3$で表されるペロブスカイト型酸化物及びLa_2CuO_4等で代表される結晶構造を有し、通常、化学式A_2BO_4で表されるペロブスカイト類似型酸化物（以下、これらペロブスカイト型とペロブスカイト類似型酸化物を総称してペロブスカイト類酸化物と呼ぶことがある。）は、それぞれの化合物が持つ電気的、化学的、物理的性質等の諸々の性質を生かして種々の用途に用いられている。特に、化学的性質を生かした応用においては、脱硝反応、酸化反応、還元反応、酸化脱水素反応、水素化反応等の触媒として用いられる。

【０００３】こうした触媒への応用においては、活性の点から一般に表面積の大きい触媒が望ましいが、これらペロブスカイト類酸化物の合成には通常高温が必要であり、そのままではシンタリングを起こしやすいため高表面積の触媒とすることは困難である。そこで、これらペロブスカイト類酸化物を適当な耐熱性を有する担体に担持し、十分な表面積を確保するとともに耐久性を向上させ、高性能の触媒（担持触媒）とする試みがなされている。

【０００４】そのような担持ペロブスカイト類酸化物触媒の調製技術としては、従来から種々の方法が提案されており、例えば、特開平３－７７６４４号公報には、ペロブスカイト型酸化物粒子を予め調製し、該粒子と希土類元素酸化物（酸化セリウムや酸化ランタン等）を無機バインダー（アルミナゾルやシリカゾル等）とともにコーディエライトやムライト等の耐熱性構造担体（ハニカム成形体）に担持するという調製技術が開示されている。しかしながら、この従来法のように固体粒子を担持するという方法では、一般に担持成分の高分散化が難しく、それゆえ、担持ペロブスカイト類酸化物の表面積を十分に大きくすることができない。したがって、こうした方法では、たとえ耐久性を向上したとしても、触媒活性の向上には限界がある。

【０００５】一方、特開平１－１６８３４３号公報には、ペロブスカイト型酸化物の調製原料である金属化合物（硝酸塩）の水溶液をハニカム型構造担体等の担体に含浸し、焼成することによって担持ペロブスカイト型酸化物触媒を得るという調製法が記載されている。しかしながら、このような水溶液の含浸による方法では、ペロブスカイト型酸化物の分散度は、一般に上記の固体粒子を担持する方法に比べて向上するものの、なお十分とは言いがたい。特に、この方法ではペロブスカイト型酸化物を生成させるための温度（焼成温度）が通常７００℃以上と高く、このためシンタリング等により担体上に生成するペロブスカイト型酸化物の表面積が低下してしまうことも欠点となっている。したがって、このような水溶液からの含浸法による方法も、結局は触媒活性の向上という点でなお改善の余地を残している。

【０００６】

【発明が解決しようとする課題】本発明の目的は、所望の種々の担体上にペロブスカイト型酸化物あるいはペロブスカイト類似型酸化物すなわちペロブスカイト類酸化物を高分散状態（高表面積）に安定に担持する方法を開発し、例えば、脱硝酸反応、完全酸化反応等の排ガス浄化処理反応をはじめとする各種の触媒反応に対して、優れた触媒活性及び耐久性等を発揮する多種多様な組成及び性状の高性能のペロブスカイト類酸化物担持触媒を容易にしかも安価に製造する方法を提供することにある。

【０００７】

【課題を解決するための手段】本発明者らは、前記従来技術における種々の問題点を解決し、前記目的を達成すべく鋭意研究を行った結果、所望のペロブスカイト型酸化物あるいはペロブスカイト類似型酸化物の調製原料である金属化合物（金属塩及び／又は金属錯体）をエーテル結合を持つアルコールと窒素含有アルコールからなる溶媒という特定の成分からなる混合溶媒に溶解し、これを適当な担体（特に耐熱性を有する酸化物系担体）に含浸させ担持し、しかる後に適当な温度で熱分解（焼成）することによって該担体上に所定のペロブスカイト類酸化物を形成させるという新規な方法によって前記目的を満足に達成することができることを見いだした。すなわち、このように特定の調製技術を用いることによって所定の各種の担体上に所望の各種の組成のペロブスカイト型酸化物やペロブスカイト類似型酸化物を十分に分散性よくかつ安定に形成担持することに成功し、触媒活性及び耐久性等に優れた各種の担持触媒を低コストで容易に得ることができることが判明した。なお、この方法によ

れば、ペロブスカイト類酸化物のみが担持された触媒に限らず、目的に応じて更に各種の触媒成分（例えば、貴金属粒子や他の酸化物成分等）を添加した多種多様な高性能の担持ペロブスカイト類酸化物系触媒も容易に得ることができる。そして、このようにして製造した各種の担持触媒が、例えば、脱硝反応、COや炭化水素類の酸化（除去）反応等の排ガス浄化処理反応、酸化脱水素反応、水素化反応等の各種の触媒反応に対して、従来法により調製した触媒と比べて高い活性、高い耐久性を示し、有利に利用することができることも確認した。

【0008】本発明者らは、主として、これらの知見及び事実に基づいて本発明を完成するに至った。

【0009】すなわち、本発明は、エーテル結合を持つアルコールと窒素含有アルコールからなる溶媒に少なくともペロブスカイト型あるいはペロブスカイト類似型酸化物の形成原料である金属塩及び／又は金属錯体を溶解してなる溶液を担体に含浸し、熱分解することを特徴とするペロブスカイト型又はペロブスカイト担持類似型酸化物担持触媒の製造方法を提供するものである。

【0010】本発明の方法において、担体上に形成させる前記ペロブスカイト型酸化物及びペロブスカイト類似型酸化物（すなわち、ペロブスカイト類酸化物）の種類としては、特に制限はなく、公知のものなど多種多様なものを対象とすることができ、これらは目的に応じて選択され1種又は2種以上を各種の担体上に分散よく形成担持することができる。すなわち、担体上には所望の組成のペロブスカイト型酸化物を1種又は2種以上形成し担持してもよいし、所望の組成のペロブスカイト類似型酸化物を1種又は2種以上形成し担持してもよいし、また、1種又は2種以上のペロブスカイト型酸化物と1種又は2種以上のペロブスカイト類似型酸化物とを形成し担持してもよい。また、後述のようにこれらペロブスカイト類酸化物以外の他の触媒成分を同時にあるいはその前後のいずれかの過程で添加若しくは担持してもよい。

【0011】前記ペロブスカイト型酸化物は、いわゆる化学式ABO_3で代表されるペロブスキー石型あるいはそれと同様の構造（原子配置）を有することによって特徴づけられる複合酸化物である。一方、前記ペロブスカイト類似型酸化物は、例えば$Ba_2Ti_9O_{20}$やLa_2CuO_4等のいわゆるペロブスカイト類似型酸化物に分類あるいは位置付けられるものであって、通常、化学式A_2BO_4で表される複合酸化物である。ただし、これらは、A及びBが共に1種単独の金属元素であるものに限定されるものではなく、A及びBのうちのいずれか一方が2種以上の金属元素（若しくは金属イオン種）からなるものやA及びBが共に2種以上の金属元素（若しくは金属イオン種）からなるものなど金属の種類及び組み合わせ等に応じて、また、格子欠陥の有無やその濃度に応じて多種多様なものが知られているが、いずれでもよい。

【0012】本発明において、前記ペロブスカイト型酸化物又はペロブスカイト類似型酸化物の種類としては、特に制限はなく、目的等に応じて1種又は2種以上を触媒の構成成分として選択することができる。すなわち、ペロブスカイト型酸化物及びペロブスカイト類似型酸化物には、金属の種類、その組み合わせ、組成、格子欠陥の有無及び濃度などによって各種のものがあるが、本発明においては、どのようなものを対象として選んでもよい。このペロブスカイト型酸化物及びペロブスカイト類似型酸化物の構成成分となりうる金属としては、種々のものがあり、代表的なものを具体的に示すと、例えば、La、Co、Sr、Mn、Cr、Ni、Al、Ti、Ba、Ca、Fe、Bi、Pb、V、Ru、Cu、Y、In、Cd、Gd、Ga、Ge、Sm、Zr、Sn、Ce、Se、Te、W、Ta、Nb、B、Mg、Moなどを挙げることができる。

【0013】ペロブスカイト型酸化物の種類の具体例としては、例えば、$LaCoO_3$、$SrCoO_3$や$La_{1-x}Sr_xCoO_3$［下付きのx及びyは0～1の有理数を表す。以下同様。］等のLa（Sr）CoO_3［ここで、（　）内の金属は置換金属を意味する。以下、同様。］、$LaMnO_3$、$SrMnO_3$や$La_{1-x}Sr_xMnO_3$等のLa（Sr）MnO_3、$LaNiO_3$、$SrNiO_3$、La（Sr）NiO_3、$CaCoO_3$、La（Ca）CoO_3、$LaFeO_3$、$SrFeO_3$、La（Sr）FeO_3、$La_{1-x}Sr_xCo_{1-y}Fe_yO_3$等のLa（Sr）Co（Fe）$O_3$、La（Ba）$MnO_3$、La（Ca）$MnO_3$、$LaCuO_3$、$BaCeO_3$、$BaTiO_3$、$BaSnO_3$、$CaVO_3$、$CaRuO_3$、$SrRuO_3$、Sr（Pt）$RuO_3$、$SrCeO_3$、$BaPb_{1-x}Bi_xO_3$、$CaTiO_3$、$CaZrO_3$、$CaTi_{1-x}Al_xO_3$など、更には、これら各種のペロブスカイト型酸化物に更に異種の金属原子が置換してなるものなど、多種多様な組成のものを挙げることができる。これらの中でも、La系のペロブスカイト型酸化物が特に好適に使用される。

【0014】ペロブスカイト類似型酸化物の種類の具体例としては、例えば、$La_{2-x}Sr_xCrO_4$［下付きのxは0～2の有理数を表す。以下同様。］等のLa（Sr）CrO_4［ここで、（　）内の金属は置換金属を意味する。以下、同様。］、La（Sr）AlO_4、La（Ba）FeO_4、La（Ba）AlO_4、La_2CuO_4、Ce（Ba）AlO_4、La（Sr）GaO_4など、更には、これら各種のペロブスカイト類似型酸化物に更に異種の金属原子が置換してなるものなど、多種多様な組成のものを挙げることができる。これらの中でも、La系のペロブスカイト類似型酸化物が特に好適に使用される。

【0015】本発明においては、前記ペロブスカイト型酸化物あるいはペロブスカイト類似型酸化物を担体上に

形成し担持するにあたって．これらの形成原料となる所定の金属化合物（金属塩及び／又は金属錯体）を前記特定の混合溶媒すなわちエーテル結合を持つアルコールと窒素含有アルコールからなる溶媒に溶解した溶液を適当な担体に含浸して担持するという特定の担持技法を用いることが重要である。

【００１６】本発明の方法においては．前記ペロブスカイト型酸化物又はペロブスカイト類似型酸化物の形成原料として使用する原料金属化合物としては、各種の金属塩及び／又は金属錯体を使用することができる。この金属塩．金属錯体の種類としては、ペロブスカイト型酸化物の構成成分となりうる金属の塩又は錯体であって、かつ．前記溶媒に溶解可能なものであれば特に制限はなく．どのようなものでも使用可能である。すなわち、この塩又は錯体について金属の種類としても特に制限はなく．具体的には．例えば．前記例示の各種の金属を挙げることができる。また、塩又は錯体の種類としても特に制限はなく、その代表的なものを具体的に示すと．例えば．硝酸塩、炭酸塩、硫酸塩等の無機系酸素酸塩．塩酸塩．クロロ金属酸、その塩類等のハロゲン化物類など各種の無機系塩又は錯塩類．酢酸塩、蓚酸塩等のカルボン酸塩．アセチルアセトナート等の有機金属錯体など各種の有機系塩又は錯体類などを挙げることができる。これらの中でも、特に好ましい塩類の例として、例えば、酢酸塩．硝酸塩などを挙げることができる。

【００１７】溶媒又はその成分として用いる前記エーテル結合を持つアルコールとしては、分子中に少なくとも１個のエーテル結合を持ちかつ少なくとも１個のアルコール性水酸基を有する有機化合物であれば特に制限はなく．多種多様なのものがあるが、その代表的なものを具体的に示すと．例えば、２－メトキシエタノール．２－エトキシエタノール等のセルソルブ．エチレングルコールモノアルキルエーテル類．２－（２－ブトキシエトキシ）エタノール．１－ブトキシ－２－プロパノール、１．３－ジエトキシ－２－プロパノール、メトキシベンジルアルコール等のアルコキシアルカノール類．ジエチレングリコールモノｎ－ヘキシルエーテル、ヘプタエチレングリコールモノｎ－ドデシルエーテル等のポリエチレングリコールモノアルキルエーテル類、フルフリルアルコール、テトラヒドロフルフリルアルコール．テトラヒドロピランエタノール．４－（２－ヒドロキシエチル）モルホリン等の環状エーテル系アルコール類などを挙げることができる。これらの中でも．特に、２－メトキシエタノール．２－エトキシエタノールなどが好適に使用される。なお、これらは１種又は２種以上を溶媒又はその成分として使用することができる。

【００１８】溶媒又はその成分として使用する前記窒素含有アルコールとしては．分子中に少なくとも１個の窒素原子を持ちかつ少なくとも１個のアルコール性水酸基を有するものであれば特に制限はなく．多種多様なのものがあるが、その代表的なものを具体的に示すと．例えば．ジエタノールアミン．トリエタノールアミン．ジイソプロパノールアミン、２－アミノエタノール．３－アミノ－１－プロパノール．３－ジメチルアミノ－１－プロパノール、Ｎ－メチルエタノールアミン、１－アミノシクロペンタンメタノール．２－アミノ－２－メチル－１．３－プロパンジオール等のアルカノールアミン若しくはアミノアルコール類．ヒドロキシジエチルイミノ二酢酸等のイミノアルコール類、ヒドロキシピリジン、ヒドロキシメチルピリジン．ピリジン－２－エタノール、ピペリジンエタノール等の環状アミノアルコール類、Ｎ－ヒドロキシメチルアクリルアミド等のヒドロキシアミド類などを挙げることができる。これらの中でも．特に．ジエタノールアミン．トリエタノールアミン．３－アミノ－１－プロパノールなどが好適に使用される。なお．これらは１種又は２種以上を溶媒又はその成分として使用することができる。

【００１９】本発明の方法においては．前記溶媒として．前記エーテル結合を持つアルコールと前記窒素含有アルコールとを互いに混合しないものを使用することができるが、通常は、少なくとも１種の前記エーテル結合を持つアルコールと少なくとも１種の前記窒素含有アルコールとを混合してなる混合溶媒が好適に使用される。その混合割合としては、前者と後者の合計量を１００重量部として計算して、前記の割合が．通常、０．００３～９０重量部．特に、０．１～７０重量部の範囲に選定するのが好ましい。このように、エーテル結合を持つアルコールと窒素含有アルコールを含む混合溶媒を用いることによって．より広範囲（多種多様）の金属塩及び／又は金属錯体を十分な濃度まで溶解することができる。なお．使用する溶媒若しくは溶液には．前記エーテル結合を持つアルコールや窒素含有アルコール以外の他の成分を含有させてもよく、これによって．例えば．溶解性を更に向上させるなどの処置を適宜施すことができる。

【００２０】また、担持後の熱分解（焼成）温度を比較的低温（例えば．３５０～７００℃）に設定してもペロブスカイト類酸化物を容易に生成させることができ、また．高分散状態で安定性よく担持することができる。

【００２１】なお、使用する溶媒若しくは溶液には、必要に応じて、前記エーテル結合を持つアルコールや窒素含有アルコール以外の他の成分を含有させてもよく、例えば．酢酸等の酸や一般のアミン等のアルカリなどを添加し．原料金属成分の溶解性を更に向上させるなどの処置を適宜施す方法も好適に採用することができる。

【００２２】本発明の方法においては．所定の原料金属化合物（前記金属塩及び／又は金属錯体）を、前記混合溶媒に溶解し．含浸担持用の溶液を調製し、該溶液を所定の担体に含浸させ、担持する。ここで溶解させた溶液中における原料金属化合物成分の濃度は、低くてもよいが．通常、０．００１モル／１以上にするのが好まし

い。なお、原料金属化合物の溶解を十分に達成させるためには、溶解させる原料金属化合物の金属１モル当たり、窒素含有アルコールが通常０．５モル量以上となるように混合溶媒の組成及び使用割合を選定するのが好ましい。また、使用する原料金属化合物の溶媒へ溶解度が極端に低い場合には、例えば、酢酸、アミン等のアルカリなどを適宜添加し溶解させてもよい。更に、溶解後、溶液を加熱するなどして溶媒を蒸発させて濃縮し、濃度を調節する方式もしばしば好適に採用される。また、溶媒若しくは溶液中に適宜、水若しくは水分を添加してよく、その際加水分解を起こしてもよい。

【００２３】また、前記含浸担持用の溶液には、所定のペロブスカイト類酸化物の形成原料となる前記金属成分の他に、必要に応じて更に、目的とする触媒反応に対する触媒性能の改善等を考慮して、各種の（助）触媒成分となるような添加成分を含有させてもよく、例えば、Ｐｔ、Ｐｄ、Ａｕ、Ｒｈ、Ａｇ、Ｉｒ等の貴金属成分や焼成後ペロブスカイト類酸化物とは分相するような酸化物（例えば、CeO_2、La_2O_3、Nd_2O_3、Ｍｎ酸化物、Ｃｕ酸化物、Ｃｏ酸化物、鉄酸化物、ZrO_2、Al_2O_3、SiO_2等）を生成する原料などを含有させてもよい。なお、これらの添加成分は、前記溶媒に溶解させて使用してもよいし、場合によっては溶解させないで使用してもよい。

【００２４】また、前記含浸液を調製するにあたって各溶媒成分と金属成分等の各成分の混合の順序は特に制限はない。

【００２５】前記担体としては、特に制限はなく、目的に応じて多種多様なものを使用することができるが、通常、少なくとも熱分解（焼成）時に十分な耐熱性を有するものを用いるのがよく、一般に耐熱性を有する酸化物系の担体が好適に使用される。

【００２６】そのような担体として多種多様なものがあるが、その代表的なものを示すと、例えば、コーディエライト、ムライト等の耐熱性セラミック類、アルミナ、シリカ、シリカアルミナ、チタニア、シリカチタニア、シリカマグネシア、アルミナマグネシア、アルミナボリア、マグネシア、ゼオライトなどを例示することができる。

【００２７】担体の形状としても特に制限はなく、例えば、ペレット状、ビーズ状、リング状、粉末状、顆粒状、シート状、繊維状などはもとより、クロス状、ハニカム状等のモノリス構造体などの種々の形状若しくは構造のものとして使用することができる。なお、例えばコーディエライト、ムライト等のセラミック系構造担体（モノリス等）などにアルミナやチタニア等の触媒担体成分をコーティングしたもの等の複合担体なども適宜好適に利用される。

【００２８】どのような種類及び形状の担体が好適になるかは、一般に、対象とする触媒反応の種類や他の条件によって異なるので適宜目的に応じて選定すればよい。

【００２９】前記含浸担持用溶液を担体に含浸する手法としては、特に制限はなく、従来から触媒調製等の分野において利用される含浸法（例えば、加熱含浸法、浸漬法、ディッピング法、蒸発乾固法、真空含浸法やフリーズドライ方式、スプレー方式、スピンコート方式あるいはウォッシュコート方式による含浸法等）などの多種多様な含浸方式が適用可能である。ただし、本発明の方法では、非水溶液を含浸するので、この点を考慮して行う。

【００３０】本発明の方法においては、前記所定の溶液を所定の担体に含浸し、少なくとも前記ペロブスカイト類酸化物の前駆体となる金属成分を担持した後、熱分解を行い、該担体上で金属成分（原料金属化合物又はその誘導体）を所定のペロブスカイト類酸化物に転化させ、少なくとも所望のペロブスカイト類酸化物が分散性よく担持された担持触媒を得る。この熱分解は、通常、１００℃以上で乾燥し、３００～１５００℃、好ましくは、３５０～８５０℃の温度で焼成することによって達成される。その際、焼成温度が例えば３００℃未満というようにあまり低いと所望のペロブスカイト類酸化物が形成できなかったり、形成に長時間を有することがある。一方、あまり高温で焼成すると担持成分と担体との好ましくない反応が起こったり、あるいは、シンタリングによる表面積の低下などを起こしやすい。こうしたシンタリングを極力避けるために、例えば３５０～７００℃程度というより低温で焼成することも好適に採用される。

【００３１】なお、乾燥は通常の加熱乾燥で行ってもよいし、熱風による乾燥、減圧による乾燥などによってもよいし、どのような方法によってもよい。乾燥工程は、場合によっては省略することもできる。

【００３２】また、前記焼成は、通常、空気又は酸素含有ガス雰囲気下で行う。好適な焼成時間は、温度等によって異なるが、通常、０．１～１００時間程度である。

【００３３】以上のようにして、所定の担体上に少なくとも所望のペロブスカイト類酸化物が分散性よく安定に担持されている各種の担持ペロブスカイト類酸化物触媒を効率よく得ることができる。なお、この担持触媒は、前記したように、ペロブスカイト類酸化物のほかに、他の触媒成分等の添加成分が担持含有されている多種多様な組成のものとすることができる。また、こうした（助）触媒成分等の添加は、前記含浸担持溶液から添加する方法に限定されるものではなく、任意の調製段階において添加することができる。例えば、前記所定の含浸溶液を含浸させる前に担体に担持等によって添加してもよいし、該含浸後に担持添加してもよいし、前記乾燥後あるいは焼成後に添加し担持してもよい。これらの添加物の担持は、通常の水溶液等からの含浸法などによっても好適に行うことができる。

【００３４】以上のようにして、目的とする各種の触媒

反応に好適な多種多様な組成の担持ペロブスカイト類酸化物触媒を容易に製造することができる。

【0035】このようにして本発明の方法によって製造した各種の担持ペロブスカイト類酸化物触媒は、酸化反応、還元反応等の多種多様な触媒反応に利用することができるが、中でも特に、例えば、自動車排気ガスやボイラー等の廃ガスの浄化等において重要な脱硝反応（NO_xの還元除去反応：この場合、還元剤としては多種多様なもの、例えば、アンモニア、尿素、CO、炭化水素等の有機物、あるいはこれらの混合物などを用いることができる。）、COや炭化水素（例えば、メタン、エタン、プロパン等の飽和炭化水素、エチレン、アセチレン、プロピレン、ブテン等の不飽和炭化水素、ベンゼン、トルエン、キシレン等の芳香族炭化水素等）、含酸素有機化合物（例えば、アルデヒド類、アルコール類、カルボン酸類、エーテル類等）、含硫黄化合物（例えば、メルカプタン類、チオフェン類等）、含窒素化合物（例えば、アミン類、アンモニア等）などの完全酸化処理や部分酸化反応など、炭化水素（特に、飽和炭化水素）等の酸化脱水素反応、不飽和炭化水素や芳香族炭化水素等の水素化反応、飽和炭化水素、不飽和炭化水素、芳香族炭化水素等の水素化分解反応など各種の重要な反応に対して好適に利用することができる。

【0036】

【実施例】以下に、本発明の実施例及びその比較例を示し、これらによって本発明を具体的に説明するが、本発明はこれらの実施例に限定されるものではない。

【0037】実施例1

[触媒調製] 2－メトキシエタノール600重量部とジエタノールアミン330重量部との混合溶媒に、酢酸ランタン水和物（含水率7．9重量%）35重量部を溶解した後、酢酸コバルト4水和物25重量部を溶解し、よく撹拌し含浸溶液を調製した。

【0038】この含浸溶液をコーディエライト製のハニカム状成形担体に含浸させ、その後、150℃で5時間乾燥し、次いで、600℃で2時間空気焼成し、該ハニカム担体の面上に$LaCoO_3$ペロブスカイト型酸化物が0．15g／ccの担持率で形成担持された所望の担持触媒（触媒1）を得た。

【0039】なお、$LaCoO_3$ペロブスカイト型酸化物の形成は、該触媒の一部を粉砕し、これをX線回折測定することによって確認した。

【0040】[触媒活性評価] 次に、上記で得た触媒1を触媒として用い、下記の条件でトルエンの酸化反応（CO_2とH_2Oへの完全酸化反応）を行い、各温度におけるトルエンの転化率を測定し該触媒の活性及び性能を評価した。なお、この活性試験は、まず、600℃で2時間予備反応を行い触媒活性を安定化させてから、反応温度を低温から高温へ段階的に上昇させることによって行った。このようにして測定した所定の各反応温度における

トルエンの転化率を表1に示す。

【0041】反応条件：

反応方式：高圧流通法

供給ガス組成：トルエン500ppm；酸素21%；窒素バランス

空間速度（GHSV）：50，000h^{-1}

反応温度：200～350℃；ただし、予備反応は600℃（2h）

【0042】実施例2

[触媒調製] 2－エトキシエタノール700重量部とトリエタノールアミン150重量部との混合溶媒に、酢酸ランタン水和物（含水率7．9重量%）35重量部を溶解した後、酢酸コバルト4水和物25重量部を溶解し、よく撹拌し含浸溶液を調製した。

【0043】この含浸溶液をコーディエライト製のハニカム状成形担体に含浸させ、その後、150℃で5時間乾燥し、次いで、550℃で2時間空気焼成し、該ハニカム担体の面上に$LaCoO_3$ペロブスカイト型酸化物が0．14g／ccの担持率で形成担持された所望の担持触媒（触媒2）を得た。

【0044】なお、$LaCoO_3$ペロブスカイト型酸化物の形成は、該触媒の一部を粉砕し、これをX線回折測定することによって確認した。

【0045】[触媒活性評価] 次に、上記で得た触媒2を触媒として用い、下記の条件でNOのアンモニアによる還元反応を行い、各温度におけるNOの転化率を測定し該触媒の活性及び性能を評価した。なお、この活性試験は、まず、600℃で2時間予備反応を行い触媒活性を安定化させてから、反応温度を低温から高温へ段階的に上昇させることによって行った。このようにして測定した所定の各反応温度におけるNOの転化率を表2に示す。

【0046】反応条件：

反応方式：高圧流通法

供給ガス組成：NO 200ppm；SO_2 100ppm；NH_3 200ppm；酸素10%；H_2O 5%；窒素バランス

空間速度（GHSV）：30，000h^{-1}

反応温度：300～400℃；ただし、予備反応は600℃（2h）

【0047】実施例3

[触媒調製] 酢酸ランタン水和物（含水率7．9重量%）35重量部、酢酸ストロンチウム22重量部をそれぞれ、別々に用意した2－メトキシエタノール880重量部とトリエタノールアミン340重量部との混合溶媒に溶解し、それぞれの溶液を調製した。次に、モル比La：Sr：Co＝4：1：5になるように上記それぞれの溶液をとり、これらを混合し、含浸溶液とした。

【0048】この含浸溶液をコーディエライト製のハニ

カム状成形担体に含浸させ．その後．１５０℃で５時間乾燥し、次いで．６００℃で２時間空気焼成し．該ハニカム担体の面上に$La_{0.8}Sr_{0.2}CoO_3$ペロブスカイト型酸化物が０．１４ｇ／ｃｃの担持率で形成担持された所望の担持触媒（触媒３）を得た。

【００４９】なお、$La_{0.8}Sr_{0.2}CoO_3$ペロブスカイト型酸化物の形成は、該触媒の一部を粉砕し．これをＸ線回折測定することによって確認した。

【００５０】［触媒活性評価］上記で得た触媒３を触媒として用いて実施例２と同様の方法・条件でＮＯのアンモニアによる還元反応を行い、その活性を評価した。この結果を表２に示す。

【００５１】実施例４

［触媒調製］２－メトキシエタノール６００重量部とジエタノールアミン３３０重量部との混合溶媒に．酢酸ランタン水和物（含水率７．９重量%）３５重量部を溶解した後、酢酸第二銅無水和物９重量部を溶解し．よく攪拌し含浸溶液を調製した。

【００５２】この含浸溶液をペレット状のγ－アルミナ担体に含浸させ．その後．１５０℃で５時間乾燥し、次いで．５５０℃で２時間空気焼成し．該ペレット状のγ－アルミナ担体の面上にLa_2CuO_4ペロブスカイト類似型酸化物が０．１５ｇ／ｃｃの担持率で形成担持された所望の担持触媒（触媒４）を得た。

【００５３】なお、La_2CuO_4ペロブスカイト類似型酸化物の形成は．該触媒の一部を粉砕し、これをＸ線回折測定することによって確認した。

【００５４】［触媒活性評価］上記で得た触媒４を触媒として用いて実施例１と同様の方法・条件でトルエンの酸化反応を行い．その活性を評価した。この結果を表１に示す。

【００５５】比較例１

［触媒調製］硝酸ランタン６水和物８８重量部と硝酸コバルト６水和物５０重量部を純水５００重量部に溶解した。この水溶液に、水酸化ナトリウム６１重量部を純水５００重量部に溶解した溶液を攪拌しながら徐々に添加し．沈殿を生成させた。この沈殿をろ過により回収し、水洗した後、１５０℃で５時間乾燥し．次いで．７００℃で空気焼成し．粉末状の$LaCoO_3$ペロブスカイト型酸化物を得た。

【００５６】次に、該$LaCoO_3$ペロブスカイト型酸＊化物粉末１０重量部に粉末状のγ－アルミナ１００重量部と純水１００重量部を添加し、ボールミルにて１０時間混合し、得られた混合物を、適宜水分調整した後、コーディエライト製のハニカム状成形担体にウォッシュコート法によって担持（コーティング）した。その後．１５０℃で５時間乾燥し、次いで、８００℃で３時間空気焼成し．該ハニカム担体の面上に$LaCoO_3$ペロブスカイト型酸化物とアルミナからなる固形分が０．１８ｇ／ｃｃの担持率で担持された比較例としての担持触媒（触媒Ｒ１）を得た。

【００５７】［触媒活性評価］上記で得た触媒Ｒ１を触媒として用いて実施例１と同様の方法・条件でトルエンの酸化反応を行い、その活性を評価した。この結果を表１に示す。

【００５８】比較例２

［触媒調製］硝酸ランタン６水和物８９重量部と硝酸マンガン４水和物３５重量部を純水５００重量部に溶解した。この水溶液に、水酸化ナトリウム６１重量部を純水５００重量部に溶解した溶液を攪拌しながら徐々に添加し．沈殿を生成させた。この沈殿をろ過により回収し、水洗した後、１５０℃で５時間乾燥し．次いで．７００℃で空気焼成し．粉末状の$LaMnO_3$ペロブスカイト型酸化物を得た。

【００５９】次に、該$LaMnO_3$ペロブスカイト型酸化物粉末１０重量部に粉末状のγ－アルミナ１００重量部と純水１００重量部を添加し、ボールミルにて１０時間混合し、得られた混合物を、適宜水分調整した後、コーディエライト製のハニカム状成形担体にウォッシュコート法によって担持（コーティング）した。その後．１５０℃で５時間乾燥し、次いで、８００℃で３時間空気焼成し．該ハニカム担体の面上に$LaMnO_3$ペロブスカイト型酸化物とアルミナからなる固形分が０．１０ｇ／ｃｃの担持率で担持された比較例としての担持触媒（触媒Ｒ２）を得た。

【００６０】［触媒活性評価］上記で得た触媒Ｒ２を触媒として用いて実施例２と同様の方法・条件でＮＯのアンモニアによる還元反応を行い、その活性を評価した。この結果を表２に示す。

【００６１】

【表１】

触媒		転化率／%			
		200℃	250℃	300℃	350℃
実施例１	触媒１	82.0	98.2	100	100
実施例４	触媒４	80.2	97.8	100	100
比較例１	触媒Ｒ１	71.8	89.0	97.8	100

【００６２】

【表２】

触媒		転化率／%		
		300℃	350℃	400℃
実施例2	触媒2	81.1	92.3	63.0
実施例3	触媒3	87.3	93.8	94.5
比較例2	触媒R2	71.0	85.5	78.8

【0063】表1及び表2に示す結果からも明らかなように、担体の種類やペロブスカイト類酸化物の種類を変えても、本発明の方法（前記特定の有機系混合溶媒の溶液を含浸液として担持するという担持方法を用いる方法）によって調製された担持ペロブスカイト型酸化物触媒及び担持ペロブスカイト類似型酸化物の方が、従来の水溶液を含浸液とする方法や予め得た固体粒子を担持するという方法によって調製した触媒よりも、酸化反応や還元反応に対して優れた触媒性能を有していることがわかる。このことは、本発明の方法によって調製した場合には、各種の担体上に所望の各種のペロブスカイト類酸化物をより高分散状態（高表面積）に効果的に形成担持することができることによるものであり、したがって、上記実施例に示す反応以外の他の種々の触媒反応（前記）に対しても同様に従来法によるものよりも優れた触媒性能を発揮する。実際、本発明の方法により得た各種の担持ペロブスカイト類酸化物触媒あるいはこれに更に貴金属等の他の触媒成分を担持等により添加した各種の＊

＊触媒が、上記の反応以外の前記した各種の反応に対しても優れた性能（活性、耐久性等）を示すことも確認した。

【0064】

【発明の効果】本発明の方法においては、エーテル結合を持つアルコールと窒素含有アルコールからなる混合溶媒という特定の有機系非水溶媒に所定のペロブスカイト類酸化物の形成原料となる金属塩及び／又は金属錯体を溶解してなる溶液を含浸し、熱分解するという特定の調製法（特に担持方法）を用いているので、従来の水溶液を含浸液とする方法や予め得た固体粒子を担持するという方法によって調製した場合よりも、所望の各種の担体上にペロブスカイト型酸化物あるいはペロブスカイト類似型酸化物すなわちペロブスカイト類酸化物を高分散状態（高表面積）に安定に担持することができる。したがって、本発明の方法によると、従来法によるものに比べて、NO_xの還元除去反応、炭化水素の酸化除去をはじめとする前記各種の反応に対して優れた触媒性能（活性及び耐久性）を示す多種多様な組成及び性状の担持ペロブスカイト類酸化物触媒（場合により、更に貴金属や他の酸化物等の他の触媒成分を添加した触媒）を容易に得ることができる。

【0065】すなわち、本発明によると上記のように触媒活性及び耐久性等に優れた各種の高性能の担持ペロブスカイト類酸化物触媒を容易にしかも安価に製造する方法を提供することができる。

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(54) PRODUCTION OF PEROVSKITE OR PEROVSKITE-LIKE STRUCTURE OXIDE CARRYING CATALYST

(57) Abstract:
PURPOSE: To produce the catalyst exhibiting excellent catalytic activity, durability, etc., to various catalytic reactions by impregnatipg a carrier with a soln. of a perovskite or perovskite-like structure oxide forming material in a solvent consisting of an alcohol having an ether linkage and a nitrogen-contg. alcohol and thermally decomposing the soln.
CONSTITUTION: This catalyst is produced as follows. Namely, a metallic salt and/or a metallic complex as the raw material for preparing the desired perovskite or perovskite-like structure oxide are firstly dissolved in a mixed solvent consisting of an alcohol having an ether linkage and a nitrogen-contg. alcohol. An appropriate carrier (especially an oxide carrier resistant to heat) is impregnated with the soln. which is then thermally decomposed (baked) at an appropriate temp. to form the specified perovskite-structure oxide on the carrier.

* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1]A carrier is impregnated in a solution which dissolves metal salt and/or a metal complex which are the formation raw materials of a perovskite type or a perovskite similar type oxide at least in a solvent which consists of alcohol with an ether bond, and nitrogen content alcohol, A perovskite type carrying out a pyrolysis or a manufacturing method of a perovskite similar type oxide carried catalyst.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]If this invention is said in more detail about the manufacturing method of a perovskite type or perovskite similar type oxide carried catalyst, It is related with the method of manufacturing easily the carried catalyst of the various presentations with which the perovskite type oxide and/or the perovskite similar type oxide are supported often [dispersibility] and stably at least on various kinds of oxide stock carriers, and description. The catalyst acquired by the method of this invention can be suitably used as removal catalysts, such as nitrogen oxides (NO_x), CO, and hydrocarbon (HC), a dehydrogenation catalyst, a hydrocracking catalyst catalyst, etc.
[0002]
[Description of the Prior Art]It has a PEROBU skiing stone ($CaTiO_3$) or the same crystal structure as this, It has a crystal structure represented with a perovskite type oxide, La_2CuO_4, etc. which are expressed with what is called chemical formula ABO_3, Usually, the perovskite similar type oxide expressed with chemical formula A_2BO_4. (these perovskite type and a perovskite similar type oxide may be hereafter called a perovskite oxide generically.) -- it is used for various uses taking advantage of the character of everythings, such as electric, chemical, a physical property, etc. which each compound has. In the application in which chemical nature was employed especially efficiently, it is used as catalysts, such as a denitrification reaction, oxidation reaction, a reduction reaction, oxidation dehydrogenation, and a hydrogenation reaction.
[0003]In the application to such a catalyst, although a catalyst with large surface area is generally desirable from a point of activity, an elevated temperature is usually required for composition of these perovskite oxide, and since it is easy to cause sintering, it is difficult [it] as it is to consider it as the catalyst of high surface area. Then, these perovskite oxide is supported to the carrier which has suitable heat resistance, while securing sufficient surface area, endurance is raised, and the trial made into a highly efficient catalyst (carried catalyst) is made.
[0004]As preparation art of such a support perovskite oxide catalyst, Various methods are proposed from the former, for example, to JP,3-77644,A. Perovskite type oxide particles are prepared beforehand, The preparation art of supporting these particles and rare earth element oxides (cerium oxide, a lanthanum trioxide, etc.) to heat-resistant structure carriers (honeycomb Plastic solid), such as cordierite and mullite, with inorganic binders (silica alumina sol, sol, etc.) is indicated.However, in the method of supporting a particle like this conventional method, generally, high decentralization of a support ingredient is difficult and, so, cannot enlarge surface area of a support perovskite oxide enough. Therefore, in such a method, even if it improves endurance, there will be a limit in improvement in catalytic activity.
[0005]On the other hand, to JP,1-168343,A, the method of preparation of acquiring a

support perovskite type oxide catalyst is indicated by impregnating carriers, such as a honeycomb mold structure carrier, and calcinating the solution of the metallic compounds (nitrate) which are the preparation raw materials of a perovskite type oxide. However, in the method by being impregnated of such solution, although the degree of dispersion of a perovskite type oxide improves compared with the method of generally supporting the above-mentioned particle, it is hard to say that it is still more enough. In particular, by this method, the temperature (calcination temperature) for making a perovskite type oxide generate is usually as high as not less than 700 **, and it has also become a fault that the surface area of the perovskite type oxide which is generated on a carrier by sintering etc. for this reason falls. Therefore, in addition, the method by the method of being impregnated from such solution has also left the room for an improvement in respect of improvement in catalytic activity after all.

[0006]

[Problem(s) to be Solved by the Invention]The purpose of this invention develops the method of supporting stably a perovskite type oxide or a perovskite similar type oxide, i.e., a perovskite oxide, to a high dispersion state (high surface area) on the carrier of desired versatility, For example, it is in providing the method of manufacturing easily and cheaply the various presentations and the highly efficient perovskite oxide carried catalyst of description which demonstrate outstanding catalytic activity, endurance, etc., to various kinds of catalytic reaction including exhaust gas purifying treatment reactions, such as a denitrification acid reaction and a complete oxidation reaction.

[0007]

[Means for Solving the Problem]A result of having inquired wholeheartedly this invention persons solving various problems in said conventional technology, and attaining said purpose, Metallic compounds (metal salt and/or metal complex) which are the preparation raw materials of a desired perovskite type oxide or a perovskite similar type oxide are dissolved in a mixed solvent which consists of a specific ingredient called a solvent which consists of alcohol with an ether bond, and nitrogen content alcohol, It impregnated with a suitable carrier (oxide stock carrier which has especially heat resistance), this was supported, and it found out that said purpose could be attained to satisfaction by a new method of making a predetermined perovskite oxide form on this carrier by carrying out a pyrolysis (calcination) at a suitable temperature for after an appropriate time. that is, it succeeding in fully carrying out formation support often [dispersibility] and stably, and a desired perovskite type oxide of various kinds of presentations, and a perovskite similar type oxide on a carrier of predetermined various kinds, by using preparation art specific in this way, It became clear that various kinds of carried catalysts excellent in catalytic activity, endurance, etc. could be easily acquired by low cost. According to this method, various highly efficient support perovskite oxide stock catalysts which added further various kinds of catalyst components (for example, precious-metals particles, other oxide components, etc.) not only according to a catalyst but according to the purpose that only a perovskite oxide was supported can also be acquired easily. And various kinds of carried catalysts which were carried out in this way and manufactured receive various kinds of catalytic reaction, such as exhaust gas purifying treatment reactions, such as a denitrification reaction, CO, an oxidation (removal) reaction of hydrocarbon, oxidation dehydrogenation, and a hydrogenation reaction, for example, High activity and high endurance were shown compared with a catalyst prepared with a conventional method, and it also checked that it could use advantageously.

[0008]This invention persons came to complete this invention mainly based on these knowledge and facts.

[0009]Namely, a carrier is impregnated with this invention in a solution which dissolves metal salt and/or a metal complex which are the formation raw materials of a perovskite type or a perovskite similar type oxide at least in a solvent which consists of alcohol with an ether bond, and nitrogen content alcohol, A manufacturing method of a perovskite

type carrying out a pyrolysis or a perovskite support similar type oxide carried catalyst is provided.

[0010]In a method of this invention, as a kind of said perovskite type oxide and a perovskite similar type oxide (namely, perovskite oxide) which are made to form on a carrier, There is no restriction in particular and it can be aimed at various things, such as a publicly known thing, and these are chosen according to the purpose and can improve [distribution] one sort or two sorts or more formation support on various kinds of carriers. namely, a perovskite type oxide of a presentation of a request on a carrier -- one sort -- or two or more sorts may be formed and it may support -- by carrying out. a perovskite similar type oxide of a desired presentation -- one sort -- or two or more sorts may be formed and it may support -- it may carry out, and one sort or two sorts or more of perovskite type oxides, one sort, or two sorts or more of perovskite similar type oxides may be formed and supported. Other catalyst components other than these perovskite oxide may be added or supported with one before and behind that of processes simultaneous like the after-mentioned.

[0011]Said perovskite type oxide is a multiple oxide characterized by having the same structure (atomic arrangement) as a PEROBU skiing stone type or it which is represented with what is called chemical formula ABO_3. On the other hand, said perovskite similar type oxide is what is classified or positioned, for example in what is called perovskite similar type oxides, such as Ba_2TiO_4 and La_2CuO_4, Usually, it is a multiple oxide expressed with chemical formula A_2BO_4. However, neither of these are what is limited to that A and whose B are one-sort independent metallic elements, According to a kind, combination, etc. of metal, such as what either A or the B become from two or more sorts of metallic elements (or metal ion kind), and a thing which both A and B become from two or more sorts of metallic elements (or metal ion kind), Any may be sufficient although various things are known according to existence of a lattice defect, or its concentration.

[0012]In this invention, as a kind of said perovskite type oxide or perovskite similar type oxide, there is no restriction in particular and one sort or two sorts or more can be chosen as a constituent of a catalyst according to the purpose etc. That is, although some perovskite type oxides and perovskite similar type oxides are [various kinds of] with existence, concentration, etc. of a metaled kind, its combination, a presentation, and a lattice defect, in this invention, you may also choose for what kind of thing. As metal which can serve as a constituent of this perovskite type oxide and a perovskite similar type oxide, When some are various and a typical thing is shown concretely, for example La, Co, Sr, Mn, Cr, nickel, aluminum, Ti, Ba, Ca, Fe, Bi, Pb, V, Ru, Cu, Y, In, Cd, Gd, Ga, germanium, Sm, Zr, Sn, Ce, Se, Te, W, Ta, Nb, B, Mg, Mo, etc. can be mentioned.

[0013]As an example of a kind of perovskite type oxide, $LaCoO_3$, $SrCoO_3$, and x and y with the bottom of $La_{1-x}Sr_xCoO_3$[express a rational number of 0-1, for example. It is the same as that of the following. La(Sr) CoO_3[, such as], -- here, metal in () means substitution metal. the following -- the same . La(Sr) MnO_3, such as], $LaMnO_3$, $SrMnO_3$, $La_{1-x}Sr_xMnO_3$, $LaNiO_3$, $SrNiO_3$, La(Sr) NiO_3, $CaCoO_3$, La(Ca) CoO_3, $LaFeO_3$, La(Sr) Co(Fe) O_3, such as $SrFeO_3$, La(Sr) FeO_3, and $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$, La(Ba) MnO_3, La(Ca) MnO_3, $LaCuO_3$, $BaCeO_3$, $BaTiO_3$, $BaSnO_3$, $CaVO_3$, $CaRuO_3$, $SrRuO_3$, Sr(Pt) RuO_3, $SrCeO_3$, $BaPb_{1-x}Bi_xO_3$, Things of various presentations, such as what a metal atom further of a different kind replaces by perovskite type oxides of further these various kinds, such as $CaTiO_3$, $CaZrO_3$, and $CaTi_{1-x}$aluminum$_xO_3$, can be mentioned. Also in these, a perovskite type oxide of an La system is used especially suitably.

[0014]As an example of a kind of perovskite similar type oxide, x with the bottom of La_{2-}

$_xSr_xCrO_4$[expresses a rational number of 0-2, for example. It is the same as that of the following. La(Sr) CrO_4[, such as], -- here, metal in () means substitution metal. the following -- the same .], La(Sr) AlO_4, La(Ba) FeO_4, La(Ba) AlO_4, La_2CuO_4, Ce(Ba) AlO_4, La (Sr) GaO_4, etc. further, Things of various presentations, such as what a metal atom further of a different kind replaces by a perovskite similar type oxide of these various kinds, can be mentioned. Also in these, a perovskite similar type oxide of an La system is used especially suitably.

[0015]In this invention, are in charge of forming said perovskite type oxide or a perovskite similar type oxide on a carrier, and supporting it, It is important to use a specific support technique of a suitable carrier being impregnated and supporting a solution which dissolved predetermined metallic compounds (metal salt and/or metal complex) used as these formation raw materials in a solvent which consists of alcohol with said specific mixed solvent, i.e., an ether bond, and nitrogen content alcohol.

[0016]In a method of this invention, various kinds of metal salt and/or metal complexes can be used as raw material metallic compounds used as a formation raw material of said perovskite type oxide or a perovskite similar type oxide. As a kind of this metal salt and metal complex, it is a metaled salt or a complex which can serve as a constituent of a perovskite type oxide, and if the dissolution to said solvent is possible, there is no restriction in particular and it is usable in anythings. That is, there is no restriction in particular also as a metaled kind about this salt or complex, and various kinds of metal of said illustration can be mentioned concrete, for example. If there is no restriction in particular also as a kind of a salt or complex and the typical thing is shown concretely, For example, inorganic system oxygen acid salts, such as a nitrate, carbonate, and sulfate, a hydrochloride, chloro metal acid, Various kinds of organic system salts, such as an organometallic complex, or complexes, such as carboxylate, such as various kinds of inorganic system salts, such as halogenides, such as the salts, or complex salt, acetate, and an oxalate, and acetylacetonato, etc. can be mentioned. Also in these, acetate, a nitrate, etc. can be especially mentioned as an example of desirable salts, for example.

[0017]If it is an organic compound which has at least one alcoholic hydroxyl group with at least one ether bond in a molecule as alcohol with said ether bond used as a solvent or its ingredient, there is no restriction in particular and there are various thing things, but. When the typical thing is shown concretely, for example 2-methoxyethanol, Cellosolve, such as 2-ethoxyethanol, and ethylene glucohol monoalkyl ether. 2-(2-butoxyethoxy) ethanol, 1-butoxy-2-propanol, Alkoxy alkanol, such as 1,3-diethoxy- 2-propanol and methoxybenzyl alcohol. Polyethylene-glycol monoalkyl ether, such as diethylene-glycol monon-hexyl ether and heptaethylene glycol mono- n-dodecylether. Cyclic ether system alcohols, such as furfuryl alcohol, tetrahydrofurfuryl alcohol, tetrahydropyranethanol, and 4-(2-hydroxyethyl) morpholine, etc. can be mentioned. Also in these, 2-methoxyethanol, 2-ethoxyethanol, etc. are used especially suitably. These can use one sort or two sorts or more as a solvent or its ingredient.

[0018]As said nitrogen content alcohol used as a solvent or its ingredient, if it has at least one alcoholic hydroxyl group with at least one nitrogen atom in a molecule, there is no restriction in particular and there are various thing things, but. When the typical thing is shown concretely, for example Diethanolamine, Triethanolamine, diisopropanolamine, 2-aminoethanol, 3-amino-1-propanol, 3-dimethylamino 1-propanol, N-methylethanol amine, 1-amino cyclopentane methanol, Alkanolamines or amino alcohol, such as 2-amino-2-methyl-1,3-propanediol, Imino alcohols, such as a hydroxydiethyliminodiacetic acid, hydroxypyridine, Hydroxyamide, such as annular amino alcohol, such as hydroxymethylpyridine, pyridin-2-ethanol, and piperidine ethanol, and N-hydroxymethylacrylamide, can be mentioned. Also in these, diethanolamine, triethanolamine,

3-amino-1-propanol, etc. are used especially suitably. These can use one sort or two sorts or more as a solvent or its ingredient.

[0019]Although what does not mix alcohol with said ether bond and said nitrogen content alcohol of each other can be used as said solvent in a method of this invention, Usually, a mixed solvent which mixes alcohol with said at least one sort of ether bonds and said at least one sort of nitrogen content alcohol is used suitably. calculating the total quantity of the former and the latter as 100 weight sections as the mixing ratio -- the aforementioned rate -- usually -- 0.003- it is preferred to select in the range of 0.1 to 70 weight section especially 90 weight section. Thus, more extensive (various) metal salt and/or a metal complex can be dissolved to sufficient concentration by using a mixed solvent containing alcohol with an ether bond, and nitrogen content alcohol. Other ingredients other than alcohol which has said ether bond in a solvent or a solution to be used, or nitrogen content alcohol may be made to contain, and it can deal with raising solubility further etc. suitably by this, for example.

[0020]Even if it sets pyrolysis (calcination) temperature after support as low temperature (for example, 350-700 **) comparatively, a perovskite oxide can be made to be able to generate easily, and it can support with a high dispersion state with sufficient stability.

[0021]Other ingredients other than alcohol which has said ether bond in a solvent or a solution to be used if needed, or nitrogen content alcohol may be made to contain, For example, alkali, such as acid, such as acetic acid, and general amine, etc. can be added, and a method of dealing with raising the solubility of a raw material metallic component further etc. suitably can also be adopted suitably.

[0022]In a method of this invention, predetermined raw material metallic compounds (said metal salt and/or metal complex) are dissolved in said mixed solvent, a solution for impregnating support is prepared, it impregnates with a predetermined carrier and this solution is supported. Although concentration of a raw material metallic-compounds ingredient in a solution in which it was made to dissolve here may be low, it is usually preferred to carry out in 0.001 mol/l. or more. In order to make the dissolution of raw material metallic compounds fully attain, it is preferred to select a presentation and a using rate of a mixed solvent so that per 1 mol of metal of raw material metallic compounds in which it is made to dissolve, and nitrogen content alcohol may usually be 0.5 or more molar quantity. When solubility is extremely low, alkali, such as acetic acid and amine, etc. may be suitably added to a solvent of raw material metallic compounds to be used, for example, and it may be made to dissolve in it. After the dissolution, a solvent is evaporated by heating a solution, it condenses, and a method which adjusts concentration is also adopted often suitably. In a solvent or a solution, suitably, water or moisture may be added and hydrolysis may be caused in that case.

[0023]In a solution for said impregnating support, an improvement of catalyst performance to catalytic reaction made into the purpose other than said metallic component used as a formation raw material of a predetermined perovskite oxide, etc. are further taken into consideration if needed, an addition ingredient which turns into various kinds of catalyst components (assistant) being made to contain, and. For example, an oxide which carries out phase splitting to noble metal components, such as Pt, Pd, Au, Rh, Ag, and Ir, or an after-calcination perovskite oxide. A raw material etc. which generate (for example, CeO_2 and La_2O_3, Nd_2O_3, Mn-oxide, Cu oxide, Co oxide, iron oxide, ZrO_2, and $aluminum_2O_3$, SiO_2, etc.) may be made to contain. These addition ingredients may be used making it dissolve in said solvent, and they may be used without making it dissolve depending on the case.

[0024]In preparing said impregnating liquid, an order of mixing of each ingredient, such as each solvent component and a metallic component, does not have restriction in particular.

[0025]Although there is no restriction in particular and various things can be used as

said carrier according to the purpose, a carrier of oxide stock in which using what has heat resistance sufficient at the time of a pyrolysis (calcination) usually at least has heat resistance often and generally is used suitably.
[0026]Although some are various as such a carrier, If the typical thing is shown, heat-resistant ceramics, such as cordierite and mullite, alumina, silica, a silica alumina, a titania, a silica titania, silica magnesia, alumina-magnesia, alumina boria, magnesia, zeolite, etc. can be illustrated, for example.
[0027]There is no restriction in particular also as shape of a carrier, for example, a pellet type, the shape of a bead, ring shape, powder, granularity, a sheet shaped, fibrous, etc. can be used from the first as various shape, such as monolith structures, such as cross state and honeycomb shape, or a thing of structure. Compound carriers, such as what coated ceramic system structure carriers (monolith etc.), such as cordierite and mullite, etc. with catalyst support ingredients, such as alumina and a titania, for example, etc. are used suitably.
[0028]Generally, since it changes with a kind and other conditions of the target catalytic reaction, whether a carrier of what kind of kind and shape becomes suitable should just select according to the purpose suitably.
[0029]As a technique with which a carrier is impregnated, said solution for impregnating support, The impregnating method which restriction in particular does not have and is used in fields, such as catalyst preparation, from the former. (For example, the impregnating method by the heating impregnating method, dip coating, a dipping method, the evaporating method, vacuum impregnation, a freeze-dry method, spray method, spin coat system, or a wash coat method, etc.) etc. -- various impregnating methods are applicable. However, in a method of this invention, since it is impregnated, a nonaqueous solution is performed in consideration of this point.
[0030]After supporting a metallic component with which a predetermined carrier is impregnated in said predetermined solution and which serves as a precursor of said perovskite oxide at least in a method of this invention, Perform a pyrolysis, a metallic component (raw material metallic compounds or its derivative) is made to convert into a predetermined perovskite oxide on this carrier, and a desired perovskite oxide acquires at least a carried catalyst supported with sufficient dispersibility. It dries above 100 ** and 300-1500 ** of this pyrolysis is usually preferably attained by calcinating at temperature of 350-850 **. In that case, if calcination temperature is not much low like less than 300 **, a desired perovskite oxide may be unable to be formed, or it may have a long time in formation. On the other hand, if it calcinates at an elevated temperature not much, a reaction of a support ingredient and a carrier which is not preferred will occur, or it is easy to cause a fall of surface area by sintering, etc. In order to avoid such sintering as much as possible, calcinating at low temperature is also suitably adopted, for example rather than about 350-700 **.
[0031]Desiccation may be performed by the usual stoving, and it is good by desiccation by a hot wind, desiccation by decompression, etc., and good by any methods. A drying process can also be skipped depending on the case.
[0032]Said calcination is usually performed under air or oxygen containing gas atmosphere. Although suitable firing time changes with temperature etc., it is usually about 0.1 to 100 hours.
[0033]Various kinds of support perovskite oxide catalysts with which a desired perovskite oxide is stably supported with sufficient dispersibility at least on a predetermined carrier as mentioned above can be acquired efficiently. As described above, addition ingredients other than a perovskite oxide, such as other catalyst components, can make this carried catalyst a thing of various presentations by which support content is carried out. addition of such (assistant) a catalyst component etc. is not limited to a method of adding from said impregnating support solution, and can be added in arbitrary preparation stages. For example, before impregnating with said predetermined impregnation solution, it

may add by support etc. to a carrier, and support addition may be carried out after this being impregnated, and it may add and support after said desiccation or calcination. Support of these additives can be suitably performed by a method of being impregnated from usual solution etc., etc.

[0034]A support perovskite oxide catalyst of suitable various presentations for various kinds of catalytic reaction made into the purpose as mentioned above can be manufactured easily.

[0035]Thus, although various kinds of support perovskite oxide catalysts manufactured by a method of this invention can be used for various catalytic reaction, such as oxidation reaction and a reduction reaction, It is [in / purification of waste gas, such as motor exhaust and a boiler, etc. / especially for example,] an important denitrification reaction (a reduction removal reaction of NO_x: in this case) especially. What is various as a reducing agent, for example, ammonia, urea, CO, organic matters, such as hydrocarbon, or these mixtures can be used. CO and hydrocarbon (for example, saturated hydrocarbon, such as methane, ethane, and propane,.) Unsaturated hydrocarbon, such as ethylene, acetylene, propylene, and a butene, benzene, An oxygenated organic compound, such as aromatic hydrocarbon, such as toluene and xylene. (For example, aldehyde, alcohols, carboxylic acid, ether, etc.), Sulphur-containing compounds (for example, mercaptans and thiophenes etc.), a nitrogen-containing compound. (For example, amines, ammonia, etc.) etc. -- hydrogenation reactions, such as oxidation dehydrogenation [, such as hydrocarbon (especially saturated hydrocarbon)], such as complete oxidation processing and partial oxidation reaction, unsaturated hydrocarbon, and aromatic hydrocarbon, saturated hydrocarbon, and unsaturated hydrocarbon. It can use suitably to various kinds of important reactions, such as hydrocracking reactions, such as aromatic hydrocarbon.

[0036]

[Example]Although the example of this invention and its comparative example are shown below and these explain this invention to it still more concretely, this invention is not limited to these examples.

[0037]After dissolving acetic acid lantern hydrate (7.9 % of the weight of water content) 35 weight section in the mixed solvent of example 1 [catalyst preparation] 2-methoxyethanol 600 weight section and diethanolamine 330 weight section, cobaltous acetate 4 hydrate 25 weight section was dissolved, it stirred well, and the impregnation solution was prepared.

[0038]Impregnate the honeycomb shape shaping carrier made from cordierite with this impregnation solution, and after that, at 150 **, dry for 5 hours and it ranks second, The carried catalyst (catalyst 1) of the request which carries out air calcination at 600 ** for 2 hours and by which formation support of the $LaCoO_3$ perovskite type oxide was carried out at 0.15g/cc of support rate on the field of this honeycomb carrier was acquired.

[0039]Formation of the $LaCoO_3$ perovskite type oxide pulverized this a part of catalyst, and checked it by carrying out X diffraction measurement of this.

[0040][Catalytic activity evaluation] Next, toluene was oxidized on condition of the following (complete oxidation reaction to CO_2 and H_2O), the inversion rate of toluene at each temperature was measured, using as a catalyst the catalyst 1 acquired above, and the activity and performance of this catalyst were evaluated. Since a preliminary reaction is performed at 600 ** for 2 hours and catalytic activity was stabilized first, this activity examination was done by raising reaction temperature from low temperature gradually to an elevated temperature. Thus, the inversion rate of toluene at each measured predetermined reaction temperature is shown in Table 1.

[0041]reaction condition: -- reaction method: -- ordinary pressure flow method distributed gas presentation: -- toluene 500ppm -- 21% of; oxygen; nitrogen balance space-velocity (GHSV): -- 50,000h^{-1} reaction temperature: -- 200-350**;, however a preliminary reaction -

- 600 ** (2h)
[0042]After dissolving acetic acid lantern hydrate (7.9 % of the weight of water content) 35 weight section in the mixed solvent of example 2 [catalyst preparation] 2-ethoxyethanol 700 weight section and triethanolamine 150 weight section, cobaltous acetate 4 hydrate 25 weight section was dissolved, it stirred well, and the impregnation solution was prepared.

[0043]Impregnate the honeycomb shape shaping carrier made from cordierite with this impregnation solution, and after that, at 150 **, dry for 5 hours and it ranks second, The carried catalyst (catalyst 2) of the request which carries out air calcination at 550 ** for 2 hours and by which formation support of the $LaCoO_3$ perovskite type oxide was carried out at 0.14g/cc of support rate on the field of this honeycomb carrier was acquired.
[0044]Formation of the $LaCoO_3$ perovskite type oxide pulverized this a part of catalyst, and checked it by carrying out X diffraction measurement of this.
[0045][Catalytic activity evaluation] Next, the reduction reaction by ammonia of NO was performed on the following conditions, the inversion rate of NO at each temperature was measured, using as a catalyst the catalyst 2 acquired above, and the activity and performance of this catalyst were evaluated. Since a preliminary reaction is performed at 600 ** for 2 hours and catalytic activity was stabilized first, this activity examination was done by raising reaction temperature from low temperature gradually to an elevated temperature. Thus, the inversion rate of NO at each measured predetermined reaction temperature is shown in Table 2.
[0046]reaction condition: -- reaction method: -- ordinary pressure flow method distributed gas presentation: -- NO. 200ppm;$SO_2$100 -- 10% of ppm;$NH_3$200ppm; oxygen;H_2O 5%; nitrogen balance space-velocity (GHSV): -- 30,000h^{-1} reaction temperature: -- 300-400**;, however a preliminary reaction -- 600 ** (2h)
[0047]Example 3 [catalyst preparation] acetic acid lantern hydrate (7.9 % of the weight of water content) 35 weight section, It dissolved in the mixed solvent of 2-methoxyethanol 880 weight section and triethanolamine 340 weight section which prepared independently cobaltous acetate 4 hydrate 25 weight section and strontium acetate 22 weight section, respectively, and each solution was prepared. Next, the solution of each above was taken so that it might be set to mole-ratio La:Sr:Co=4:1:5, these were mixed, and it was considered as the impregnation solution.
[0048]Impregnate the honeycomb shape shaping carrier made from cordierite with this impregnation solution, and after that, at 150 **, dry for 5 hours and it ranks second, The carried catalyst (catalyst 3) of the request which carries out air calcination at 600 ** for 2 hours and by which formation support of the $La_{0.8}Sr_{0.2}CoO_3$ perovskite type oxide was carried out at 0.14g/cc of support rate on the field of this honeycomb carrier was acquired.
[0049]Formation of the $La_{0.8}Sr_{0.2}CoO_3$ perovskite type oxide pulverized this a part of catalyst, and checked it by carrying out X diffraction measurement of this.
[0050][Catalytic activity evaluation] The reduction reaction by ammonia of NO was performed on the same method and conditions as Example 2, using as a catalyst the catalyst 3 acquired above, and the activity was evaluated. This result is shown in Table 2.
[0051]After dissolving acetic acid lantern hydrate (7.9 % of the weight of water content) 35 weight section in the mixed solvent of example 4 [catalyst preparation] 2-methoxyethanol 600 weight section and diethanolamine 330 weight section, cupric-acetate anhydrate 9 weight section was dissolved, it stirred well, and the impregnation solution was prepared.
[0052]Impregnate the gamma-alumina carrier of a pellet type with this impregnation solution, and after that, at 150 **, dry for 5 hours and it ranks second, The carried catalyst (catalyst 4) of the request which carries out air calcination at 550 ** for 2

hours and by which formation support of the La_2CuO_4 perovskite similar type oxide was carried out at 0.15g/cc of support rate on the field of the gamma-alumina carrier of this pellet type was acquired.

[0053]Formation of the La_2CuO_4 perovskite similar type oxide pulverized this a part of catalyst, and checked it by carrying out X diffraction measurement of this.

[0054][Catalytic activity evaluation] Toluene was oxidized on the same method and conditions as Example 1, using as a catalyst the catalyst 4 acquired above, and the activity was evaluated. This result is shown in Table 1.

[0055]Comparative example 1 [catalyst preparation] lanthanum nitrate 6 hydrate 88 weight section and cobalt nitrate 6 hydrate 50 weight section were dissolved in pure water 500 weight section. It added in this solution gradually, stirring the solution which dissolved sodium hydroxide 61 weight section in pure water 500 weight section, and it was made to generate precipitate. After filtration having recovered this precipitate and rinsing it, at 150 **, it dried for 5 hours, it ranked second, air calcination was carried out at 700 **, and the powdered $LaCoO_3$ perovskite type oxide was obtained.

[0056]Next, gamma-alumina 100 powdered weight section and pure water 100 weight section are added to this $LaCoO_3$ perovskite type oxide powder 10 weight section, After carrying out moisture control of the mixture obtained by mixing for 10 hours with the ball mill suitably, it was supported by the WOSHU coat method to the honeycomb shape shaping carrier made from cordierite (coating). Then, at 150 **, it dried for 5 hours, it ranked second, air calcination was carried out at 800 ** for 3 hours, and the solid content which consists of a $LaCoO_3$ perovskite type oxide and alumina on the field of this honeycomb carrier acquired the carried catalyst (catalyst R1) as a comparative example supported with the support rate which is 0.18g/cc.

[0057][Catalytic activity evaluation] Toluene was oxidized on the same method and conditions as Example 1, using as a catalyst the catalyst R1 acquired above, and the activity was evaluated. This result is shown in Table 1.

[0058]Comparative example 2 [catalyst preparation] lanthanum nitrate 6 hydrate 89 weight section and manganese nitrate 4 hydrate 35 weight section were dissolved in pure water 500 weight section. It added in this solution gradually, stirring the solution which dissolved sodium hydroxide 61 weight section in pure water 500 weight section, and it was made to generate precipitate. After filtration having recovered this precipitate and rinsing it, at 150 **, it dried for 5 hours, it ranked second, air calcination was carried out at 700 **, and the powdered $LaMnO_3$ perovskite type oxide was obtained.

[0059]Next, gamma-alumina 100 powdered weight section and pure water 100 weight section are added to this $LaMnO_3$ perovskite type oxide powder 10 weight section, After carrying out moisture control of the mixture obtained by mixing for 10 hours with the ball mill suitably, it was supported by the WOSHU coat method to the honeycomb shape shaping carrier made from cordierite (coating). Then, at 150 **, it dried for 5 hours, it ranked second, air calcination was carried out at 800 ** for 3 hours, and the solid content which consists of a $LaMnO_3$ perovskite type oxide and alumina on the field of this honeycomb carrier acquired the carried catalyst (catalyst R2) as a comparative example supported with the support rate which is 0.10g/cc.

[0060][Catalytic activity evaluation] The reduction reaction by ammonia of NO was performed on the same method and conditions as Example 2, using as a catalyst the catalyst R2 acquired above, and the activity was evaluated. This result is shown in Table 2.

[0061]

[Table 1]

触媒		転化率／%			
		200℃	250℃	300℃	350℃
実施例1	触媒1	82.0	98.2	100	100
実施例4	触媒4	80.2	97.8	100	100
比較例1	触媒R1	71.8	89.0	97.8	100

[0062]
[Table 2]

触媒		転化率／%		
		300℃	350℃	400℃
実施例2	触媒2	81.1	92.3	63.0
実施例3	触媒3	87.3	93.8	94.5
比較例2	触媒R2	71.0	85.6	78.8

[0063]Even if it changes the kind of carrier, and the kind of perovskite oxide so that clearly also from the result shown in Table 1 and 2, The direction of the support perovskite type oxide catalyst and support perovskite similar type oxide which were prepared by the method (how to use the support method of supporting the solution of said specific organic system mixed solvent as impregnating liquid) of this invention, The catalyst prepared by the method of supporting the method of using conventional solution as impregnating liquid and the particle obtained beforehand shows having the catalyst performance outstanding to oxidation reaction or a reduction reaction. This twists various kinds of perovskite oxides of a request on various kinds of carriers for formation support to be more effectively carried out to a high dispersion state (high surface area), when it prepares by the method of this invention.
Therefore, the catalyst performance superior to what is similarly depended on a conventional method to other various catalytic reaction (above) other than the reaction shown in the above-mentioned example is demonstrated.
It also checked that the performances (activity, endurance, etc.) various kinds of catalysts which added other catalyst components, such as the precious metals, by support etc. further actually excelled [performances] in various kinds of support perovskite oxide catalysts or this which was obtained by the method of this invention also to various kinds of reactions described above other than the above-mentioned reaction were shown.
[0064]
[Effect of the Invention]The solution which dissolves metal salt and/or the metal complex used as the formation raw material of a predetermined perovskite oxide in a specific organic system nonaqueous solvent called the mixed solvent which consists of alcohol with an ether bond and nitrogen content alcohol in the method of this invention is impregnated, Since the specific method of preparation (especially the support method) of carrying out a pyrolysis is used, Rather than the case where it prepares by the method of supporting the method of using conventional solution as impregnating liquid, and the particle obtained beforehand. A perovskite type oxide or a perovskite similar type oxide, i.e., a perovskite oxide, can be stably supported to a high dispersion state (high surface area) on the carrier of desired various kinds. According to the method of this invention, compared with what is depended on a conventional method Therefore, the reduction removal reaction of NO_x, The various presentations and the support perovskite oxide catalyst (catalyst which

added other catalyst components, such as the precious metals and other oxides, further by the case) of description which show the catalyst performance (activity and endurance) outstanding to said various kinds of reactions including the oxidation removal of hydrocarbon can be acquired easily.

[0065]That is, according to this invention, the method of manufacturing easily and cheaply various kinds of highly efficient support perovskite oxide catalysts which were excellent in catalytic activity, endurance, etc. as mentioned above can be provided.

[Translation done.]

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TECHNICAL FIELD

[Industrial Application]If this invention is said in more detail about the manufacturing method of a perovskite type or perovskite similar type oxide carried catalyst, It is related with the method of manufacturing easily the carried catalyst of the various presentations with which the perovskite type oxide and/or the perovskite similar type oxide are supported often [dispersibility] and stably at least on various kinds of oxide stock carriers, and description. The catalyst acquired by the method of this invention can be suitably used as removal catalysts, such as nitrogen oxides (NO_x), CO, and hydrocarbon (HC), a dehydrogenation catalyst, a hydrocracking catalyst catalyst, etc.

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PRIOR ART

[Description of the Prior Art]It has a PEROBU skiing stone ($CaTiO_3$) or the same crystal structure as this, It has a crystal structure represented with a perovskite type oxide, La_2CuO_4, etc. which are expressed with what is called chemical formula ABO_3, Usually, the perovskite similar type oxide expressed with chemical formula A_2BO_4. (these perovskite type and a perovskite similar type oxide may be hereafter called a perovskite oxide generically.) -- it is used for various uses taking advantage of the character of everythings, such as electric, chemical, a physical property, etc. which each compound has. In the application in which chemical nature was employed especially efficiently, it is used as catalysts, such as a denitrification reaction, oxidation reaction, a reduction reaction, oxidation dehydrogenation, and a hydrogenation reaction.
[0003]In the application to such a catalyst, although a catalyst with large surface area is generally desirable from a point of activity, an elevated temperature is usually required for composition of these perovskite oxide, and since it is easy to cause sintering, it is difficult [it] as it is to consider it as the catalyst of high surface area. Then, these perovskite oxide is supported to the carrier which has suitable heat resistance, while securing sufficient surface area, endurance is raised, and the trial made into a highly efficient catalyst (carried catalyst) is made.
[0004]As preparation art of such a support perovskite oxide catalyst, Various methods are proposed from the former, for example, to JP,3-77644,A. Perovskite type oxide particles are prepared beforehand, The preparation art of supporting these particles and rare earth element oxides (cerium oxide, a lanthanum trioxide, etc.) to heat-resistant structure carriers (honeycomb Plastic solid), such as cordierite and mullite, with inorganic binders (silica alumina sol, sol, etc.) is indicated. However, in the method of supporting a particle like this conventional method, generally, high decentralization of a support ingredient is difficult and, so, cannot enlarge surface area of a support perovskite oxide enough. Therefore, in such a method, even if it improves endurance, there will be a limit in improvement in catalytic activity.
[0005]On the other hand, to JP,1-168343,A, the method of preparation of acquiring a support perovskite type oxide catalyst is indicated by impregnating carriers, such as a honeycomb mold structure carrier, and calcinating the solution of the metallic compounds (nitrate) which are the preparation raw materials of a perovskite type oxide. However, in the method by being impregnated of such solution, although the degree of dispersion of a perovskite type oxide improves compared with the method of generally supporting the above-mentioned particle, it is hard to say that it is still more enough. In particular, by this method, the temperature (calcination temperature) for making a perovskite type oxide generate is usually as high as not less than 700 **, and it has also become a fault that the surface area of the perovskite type oxide which is generated on a carrier by sintering etc. for this reason falls. Therefore, in addition, the method by the method of being impregnated from such solution has also left the room for an improvement in respect of improvement in catalytic activity after all.

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EFFECT OF THE INVENTION

[Effect of the Invention]The solution which dissolves metal salt and/or the metal complex used as the formation raw material of a predetermined perovskite oxide in a specific organic system nonaqueous solvent called the mixed solvent which consists of alcohol with an ether bond and nitrogen content alcohol in the method of this invention is impregnated, Since the specific method of preparation (especially the support method) of carrying out a pyrolysis is used, Rather than the case where it prepares by the method of supporting the method of using conventional solution as impregnating liquid, and the particle obtained beforehand. A perovskite type oxide or a perovskite similar type oxide, i.e., a perovskite oxide, can be stably supported to a high dispersion state (high surface area) on the carrier of desired various kinds. According to the method of this invention, compared with what is depended on a conventional method Therefore, the reduction removal reaction of NO_x, The various presentations and the support perovskite oxide catalyst (catalyst which added other catalyst components, such as the precious metals and other oxides, further by the case) of description which show the catalyst performance (activity and endurance) outstanding to said various kinds of reactions including the oxidation removal of hydrocarbon can be acquired easily.
[0065]That is, according to this invention, the method of manufacturing easily and cheaply various kinds of highly efficient support perovskite oxide catalysts which were excellent in catalytic activity, endurance, etc. as mentioned above can be provided.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]The purpose of this invention develops the method of supporting stably a perovskite type oxide or a perovskite similar type oxide, i.e., a perovskite oxide, to a high dispersion state (high surface area) on the carrier of desired versatility, For example, it is in providing the method of manufacturing easily and cheaply the various presentations and the highly efficient perovskite oxide carried catalyst of description which demonstrate outstanding catalytic activity, endurance, etc., to various kinds of catalytic reaction including exhaust gas purifying treatment reactions, such as a denitrification acid reaction and a complete oxidation reaction.

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3. In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem]A result of having inquired wholeheartedly this invention persons solving various problems in said conventional technology, and attaining said purpose, Metallic compounds (metal salt and/or metal complex) which are the preparation raw materials of a desired perovskite type oxide or a perovskite similar type oxide are dissolved in a mixed solvent which consists of a specific ingredient called a solvent which consists of alcohol with an ether bond, and nitrogen content alcohol, It impregnated with a suitable carrier (oxide stock carrier which has especially heat resistance), this was supported, and it found out that said purpose could be attained to satisfaction by a new method of making a predetermined perovskite oxide form on this carrier by carrying out a pyrolysis (calcination) at a suitable temperature for after an appropriate time. that is, it succeeding in fully carrying out formation support often [dispersibility] and stably, and a desired perovskite type oxide of various kinds of presentations, and a perovskite similar type oxide on a carrier of predetermined various kinds, by using preparation art specific in this way, It became clear that various kinds of carried catalysts excellent in catalytic activity, endurance, etc. could be easily acquired by low cost. According to this method, various highly efficient support perovskite oxide stock catalysts which added further various kinds of catalyst components (for example, precious-metals particles, other oxide components, etc.) not only according to a catalyst but according to the purpose that only a perovskite oxide was supported can also be acquired easily. And various kinds of carried catalysts which were carried out in this way and manufactured receive various kinds of catalytic reaction, such as exhaust gas purifying treatment reactions, such as a denitrification reaction, CO, an oxidation (removal) reaction of hydrocarbon, oxidation dehydrogenation, and a hydrogenation reaction, for example, High activity and high endurance were shown compared with a catalyst prepared with a conventional method, and it also checked that it could use advantageously.

[0008]This invention persons came to complete this invention mainly based on these knowledge and facts.

[0009]Namely, a carrier is impregnated with this invention in a solution which dissolves metal salt and/or a metal complex which are the formation raw materials of a perovskite type or a perovskite similar type oxide at least in a solvent which consists of alcohol with an ether bond, and nitrogen content alcohol, A manufacturing method of a perovskite type carrying out a pyrolysis or a perovskite support similar type oxide carried catalyst is provided.

[0010]In a method of this invention, as a kind of said perovskite type oxide and a perovskite similar type oxide (namely, perovskite oxide) which are made to form on a carrier, There is no restriction in particular and it can be aimed at various things, such as a publicly known thing, and these are chosen according to the purpose and can improve [distribution] one sort or two sorts or more formation support on various kinds of carriers. namely, a perovskite type oxide of a presentation of a request on a carrier -- one sort -- or two or more sorts may be formed and it may support -- by carrying out. a

perovskite similar type oxide of a desired presentation -- one sort -- or two or more sorts may be formed and it may support -- it may carry out, and one sort or two sorts or more of perovskite type oxides, one sort, or two sorts or more of perovskite similar type oxides may be formed and supported. Other catalyst components other than these perovskite oxide may be added or supported with one before and behind that of processes simultaneous like the after-mentioned.

[0011]Said perovskite type oxide is a multiple oxide characterized by having the same structure (atomic arrangement) as a PEROBU skiing stone type or it which is represented with what is called chemical formula ABO_3. On the other hand, said perovskite similar type oxide is what is classified or positioned, for example in what is called perovskite similar type oxides, such as Ba_2TiO_4 and La_2CuO_4, Usually, it is a multiple oxide expressed with chemical formula A_2BO_4. However, neither of these are what is limited to that A and whose B are one-sort independent metallic elements, According to a kind, combination, etc. of metal, such as what either A or the B become from two or more sorts of metallic elements (or metal ion kind), and a thing which both A and B become from two or more sorts of metallic elements (or metal ion kind), Any may be sufficient although various things are known according to existence of a lattice defect, or its concentration.

[0012]In this invention, as a kind of said perovskite type oxide or perovskite similar type oxide, there is no restriction in particular and one sort or two sorts or more can be chosen as a constituent of a catalyst according to the purpose etc. That is, although some perovskite type oxides and perovskite similar type oxides are [various kinds of] with existence, concentration, etc. of a metaled kind, its combination, a presentation, and a lattice defect, in this invention, you may also choose for what kind of thing. As metal which can serve as a constituent of this perovskite type oxide and a perovskite similar type oxide, When some are various and a typical thing is shown concretely, for example La, Co, Sr, Mn, Cr, nickel, aluminum, Ti, Ba, Ca, Fe, Bi, Pb, V, Ru, Cu, Y, In, Cd, Gd, Ga, germanium, Sm, Zr, Sn, Ce, Se, Te, W, Ta, Nb, B, Mg, Mo, etc. can be mentioned.

[0013]As an example of a kind of perovskite type oxide, $LaCoO_3$, $SrCoO_3$, and x and y with the bottom of $La_{1-x}Sr_xCoO_3$[express a rational number of 0-1, for example. It is the same as that of the following. La(Sr) CoO_3[, such as], -- here, metal in () means substitution metal. the following -- the same . La(Sr) MnO_3, such as], $LaMnO_3$, $SrMnO_3$, $La_{1-x}Sr_xMnO_3$, $LaNiO_3$, $SrNiO_3$, La(Sr) NiO_3, $CaCoO_3$, La(Ca) CoO_3, $LaFeO_3$, La(Sr) Co(Fe) O_3, such as $SrFeO_3$, La(Sr) FeO_3, and $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$, La(Ba) MnO_3, La(Ca) MnO_3, $LaCuO_3$, $BaCeO_3$, $BaTiO_3$, $BaSnO_3$, $CaVO_3$, $CaRuO_3$, $SrRuO_3$, Sr(Pt) RuO_3, $SrCeO_3$, $BaPb_{1-x}Bi_xO_3$, Things of various presentations, such as what a metal atom further of a different kind replaces by perovskite type oxides of further these various kinds, such as $CaTiO_3$, $CaZrO_3$, and $CaTi_{1-x}aluminum_xO_3$, can be mentioned. Also in these, a perovskite type oxide of an La system is used especially suitably.

[0014]As an example of a kind of perovskite similar type oxide, x with the bottom of $La_{2-x}Sr_xCrO_4$[expresses a rational number of 0-2, for example. It is the same as that of the following. La(Sr) CrO_4[, such as], -- here, metal in () means substitution metal. the following -- the same .], La(Sr) AlO_4, La(Ba) FeO_4, La(Ba) AlO_4, La_2CuO_4, Ce(Ba) AlO_4, La (Sr) GaO_4, etc. further, Things of various presentations, such as what a metal atom further of a different kind replaces by a perovskite similar type oxide of these various kinds, can be mentioned. Also in these, a perovskite similar type oxide of an La system is used especially suitably.

[0015]In this invention, are in charge of forming said perovskite type oxide or a perovskite similar type oxide on a carrier, and supporting it, It is important to use a specific support technique of a suitable carrier being impregnated and supporting a solution which dissolved predetermined metallic compounds (metal salt and/or metal complex) used as these formation raw materials in a solvent which consists of alcohol with said specific mixed solvent, i.e., an ether bond, and nitrogen content alcohol.
[0016]In a method of this invention, various kinds of metal salt and/or metal complexes can be used as raw material metallic compounds used as a formation raw material of said perovskite type oxide or a perovskite similar type oxide. As a kind of this metal salt and metal complex, it is a metaled salt or a complex which can serve as a constituent of a perovskite type oxide, and if the dissolution to said solvent is possible, there is no restriction in particular and it is usable in anythings. That is, there is no restriction in particular also as a metaled kind about this salt or complex, and various kinds of metal of said illustration can be mentioned concrete, for example. If there is no restriction in particular also as a kind of a salt or complex and the typical thing is shown concretely, For example, inorganic system oxygen acid salts, such as a nitrate, carbonate, and sulfate, a hydrochloride, chloro metal acid, Various kinds of organic system salts, such as an organometallic complex, or complexes, such as carboxylate, such as various kinds of inorganic system salts, such as halogenides, such as the salts, or complex salt, acetate, and an oxalate, and acetylacetonato, etc. can be mentioned. Also in these, acetate, a nitrate, etc. can be especially mentioned as an example of desirable salts, for example.
[0017]If it is an organic compound which has at least one alcoholic hydroxyl group with at least one ether bond in a molecule as alcohol with said ether bond used as a solvent or its ingredient, there is no restriction in particular and there are various thing things, but. When the typical thing is shown concretely, for example 2-methoxyethanol, Cellosolve, such as 2-ethoxyethanol, and ethylene glucohol monoalkyl ether. 2-(2-butoxyethoxy) ethanol, 1-butoxy-2-propanol, Alkoxy alkanol, such as 1,3-diethoxy- 2-propanol and methoxybenzyl alcohol. Polyethylene-glycol monoalkyl ether, such as diethylene-glycol monon-hexyl ether and heptaethylene glycol mono- n-dodecylether. Cyclic ether system alcohols, such as furfuryl alcohol, tetrahydrofurfuryl alcohol, tetrahydropyranethanol, and 4-(2-hydroxyethyl) morpholine, etc. can be mentioned. Also in these, 2-methoxyethanol, 2-ethoxyethanol, etc. are used especially suitably. These can use one sort or two sorts or more as a solvent or its ingredient.
[0018]As said nitrogen content alcohol used as a solvent or its ingredient, if it has at least one alcoholic hydroxyl group with at least one nitrogen atom in a molecule, there is no restriction in particular and there are various thing things, but. When the typical thing is shown concretely, for example Diethanolamine, Triethanolamine, diisopropanolamine, 2-aminoethanol, 3-amino-1-propanol, 3-dimethylamino 1-propanol, N-methylethanol amine, 1-amino cyclopentane methanol, Alkanolamines or amino alcohol, such as 2-amino-2-methyl-1,3-propanediol, Imino alcohols, such as a hydroxydiethyliminodiacetic acid, hydroxypyridine, Hydroxyamide, such as annular amino alcohol, such as hydroxymethylpyridine, pyridin-2-ethanol, and piperidine ethanol, and N-hydroxymethylacrylamide, can be mentioned. Also in these, diethanolamine, triethanolamine, 3-amino-1-propanol, etc. are used especially suitably. These can use one sort or two sorts or more as a solvent or its ingredient.
[0019]Although what does not mix alcohol with said ether bond and said nitrogen content alcohol of each other can be used as said solvent in a method of this invention, Usually, a mixed solvent which mixes alcohol with said at least one sort of ether bonds and said at least one sort of nitrogen content alcohol is used suitably. calculating the total quantity of the former and the latter as 100 weight sections as the mixing ratio -- the aforementioned rate -- usually -- 0.003- it is preferred to select in the range of 0.1 to 70 weight section especially 90 weight section. Thus, more extensive (various) metal salt

and/or a metal complex can be dissolved to sufficient concentration by using a mixed solvent containing alcohol with an ether bond, and nitrogen content alcohol. Other ingredients other than alcohol which has said ether bond in a solvent or a solution to be used, or nitrogen content alcohol may be made to contain, and it can deal with raising solubility further etc. suitably by this, for example.

[0020]Even if it sets pyrolysis (calcination) temperature after support as low temperature (for example, 350-700 **) comparatively, a perovskite oxide can be made to be able to generate easily, and it can support with a high dispersion state with sufficient stability.

[0021]Other ingredients other than alcohol which has said ether bond in a solvent or a solution to be used if needed, or nitrogen content alcohol may be made to contain, For example, alkali, such as acid, such as acetic acid, and general amine, etc. can be added, and a method of dealing with raising the solubility of a raw material metallic component further etc. suitably can also be adopted suitably.

[0022]In a method of this invention, predetermined raw material metallic compounds (said metal salt and/or metal complex) are dissolved in said mixed solvent, a solution for impregnating support is prepared, it impregnates with a predetermined carrier and this solution is supported. Although concentration of a raw material metallic-compounds ingredient in a solution in which it was made to dissolve here may be low, it is usually preferred to carry out in 0.001 mol/l. or more. In order to make the dissolution of raw material metallic compounds fully attain, it is preferred to select a presentation and a using rate of a mixed solvent so that per 1 mol of metal of raw material metallic compounds in which it is made to dissolve, and nitrogen content alcohol may usually be 0.5 or more molar quantity. When solubility is extremely low, alkali, such as acetic acid and amine, etc. may be suitably added to a solvent of raw material metallic compounds to be used, for example, and it may be made to dissolve in it. After the dissolution, a solvent is evaporated by heating a solution, it condenses, and a method which adjusts concentration is also adopted often suitably. In a solvent or a solution, suitably, water or moisture may be added and hydrolysis may be caused in that case.

[0023]In a solution for said impregnating support, an improvement of catalyst performance to catalytic reaction made into the purpose other than said metallic component used as a formation raw material of a predetermined perovskite oxide, etc. are further taken into consideration if needed, an addition ingredient which turns into various kinds of catalyst components (assistant) being made to contain, and. For example, an oxide which carries out phase splitting to noble metal components, such as Pt, Pd, Au, Rh, Ag, and Ir, or an after-calcination perovskite oxide. A raw material etc. which generate (for example, CeO_2 and La_2O_3, Nd_2O_3, Mn-oxide, Cu oxide, Co oxide, iron oxide, ZrO_2, and $aluminum_2O_3$, SiO_2, etc.) may be made to contain. These addition ingredients may be used making it dissolve in said solvent, and they may be used without making it dissolve depending on the case.

[0024]In preparing said impregnating liquid, an order of mixing of each ingredient, such as each solvent component and a metallic component, does not have restriction in particular.

[0025]Although there is no restriction in particular and various things can be used as said carrier according to the purpose, a carrier of oxide stock in which using what has heat resistance sufficient at the time of a pyrolysis (calcination) usually at least has heat resistance often and generally is used suitably.

[0026]Although some are various as such a carrier, If the typical thing is shown, heat-resistant ceramics, such as cordierite and mullite, alumina, silica, a silica alumina, a titania, a silica titania, silica magnesia, alumina-magnesia, alumina boria, magnesia, zeolite, etc. can be illustrated, for example.

[0027]There is no restriction in particular also as shape of a carrier, for example, a pellet type, the shape of a bead, ring shape, powder, granularity, a sheet shaped,

fibrous, etc. can be used from the first as various shape, such as monolith structures, such as cross state and honeycomb shape, or a thing of structure. Compound carriers, such as what coated ceramic system structure carriers (monolith etc.), such as cordierite and mullite, etc. with catalyst support ingredients, such as alumina and a titania, for example, etc. are used suitably.

[0028]Generally, since it changes with a kind and other conditions of the target catalytic reaction, whether a carrier of what kind of kind and shape becomes suitable should just select according to the purpose suitably.

[0029]As a technique with which a carrier is impregnated, said solution for impregnating support, The impregnating method which restriction in particular does not have and is used in fields, such as catalyst preparation, from the former. (For example, the impregnating method by the heating impregnating method, dip coating, a dipping method, the evaporating method, vacuum impregnation, a freeze-dry method, spray method, spin coat system, or a wash coat method, etc.) etc. -- various impregnating methods are applicable. However, in a method of this invention, since it is impregnated, a nonaqueous solution is performed in consideration of this point.

[0030]After supporting a metallic component with which a predetermined carrier is impregnated in said predetermined solution and which serves as a precursor of said perovskite oxide at least in a method of this invention, Perform a pyrolysis, a metallic component (raw material metallic compounds or its derivative) is made to convert into a predetermined perovskite oxide on this carrier, and a desired perovskite oxide acquires at least a carried catalyst supported with sufficient dispersibility. It dries above 100 ** and 300-1500 ** of this pyrolysis is usually preferably attained by calcinating at temperature of 350-850 **. In that case, if calcination temperature is not much low like less than 300 **, a desired perovskite oxide may be unable to be formed, or it may have a long time in formation. On the other hand, if it calcinates at an elevated temperature not much, a reaction of a support ingredient and a carrier which is not preferred will occur, or it is easy to cause a fall of surface area by sintering, etc. In order to avoid such sintering as much as possible, calcinating at low temperature is also suitably adopted, for example rather than about 350-700 **.

[0031]Desiccation may be performed by the usual stoving, and it is good by desiccation by a hot wind, desiccation by decompression, etc., and good by any methods. A drying process can also be skipped depending on the case.

[0032]Said calcination is usually performed under air or oxygen containing gas atmosphere. Although suitable firing time changes with temperature etc., it is usually about 0.1 to 100 hours.

[0033]Various kinds of support perovskite oxide catalysts with which a desired perovskite oxide is stably supported with sufficient dispersibility at least on a predetermined carrier as mentioned above can be acquired efficiently. As described above, addition ingredients other than a perovskite oxide, such as other catalyst components, can make this carried catalyst a thing of various presentations by which support content is carried out. addition of such (assistant) a catalyst component etc. is not limited to a method of adding from said impregnating support solution, and can be added in arbitrary preparation stages. For example, before impregnating with said predetermined impregnation solution, it may add by support etc. to a carrier, and support addition may be carried out after this being impregnated, and it may add and support after said desiccation or calcination. Support of these additives can be suitably performed by a method of being impregnated from usual solution etc., etc.

[0034]A support perovskite oxide catalyst of suitable various presentations for various kinds of catalytic reaction made into the purpose as mentioned above can be manufactured easily.

[0035]Thus, although various kinds of support perovskite oxide catalysts manufactured by a method of this invention can be used for various catalytic reaction, such as oxidation

reaction and a reduction reaction, It is [in / purification of waste gas, such as motor exhaust and a boiler, etc. / especially for example,] an important denitrification reaction (a reduction removal reaction of NO_x: in this case) especially. What is various as a reducing agent, for example, ammonia, urea, CO, organic matters, such as hydrocarbon, or these mixtures can be used. CO and hydrocarbon (for example, saturated hydrocarbon, such as methane, ethane, and propane,.) Unsaturated hydrocarbon, such as ethylene, acetylene, propylene, and a butene, benzene, An oxygenated organic compound, such as aromatic hydrocarbon, such as toluene and xylene. (For example, aldehyde, alcohols, carboxylic acid, ether, etc.), Sulphur-containing compounds (for example, mercaptans and thiophenes etc.), a nitrogen-containing compound. (For example, amines, ammonia, etc.) etc. -- hydrogenation reactions, such as oxidation dehydrogenation [, such as hydrocarbon (especially saturated hydrocarbon)], such as complete oxidation processing and partial oxidation reaction, unsaturated hydrocarbon, and aromatic hydrocarbon, saturated hydrocarbon, and unsaturated hydrocarbon. It can use suitably to various kinds of important reactions, such as hydrocracking reactions, such as aromatic hydrocarbon.

[Translation done.]

* NOTICES *

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Example]Although the example of this invention and its comparative example are shown below and these explain this invention to it still more concretely, this invention is not limited to these examples.
[0037]After dissolving acetic acid lantern hydrate (7.9 % of the weight of water content) 35 weight section in the mixed solvent of example 1 [catalyst preparation] 2-methoxyethanol 600 weight section and diethanolamine 330 weight section, cobaltous acetate 4 hydrate 25 weight section was dissolved, it stirred well, and the impregnation solution was prepared.
[0038]Impregnate the honeycomb shape shaping carrier made from cordierite with this impregnation solution, and after that, at 150 **, dry for 5 hours and it ranks second, The carried catalyst (catalyst 1) of the request which carries out air calcination at 600 ** for 2 hours and by which formation support of the $LaCoO_3$ perovskite type oxide was carried out at 0.15g/cc of support rate on the field of this honeycomb carrier was acquired.
[0039]Formation of the $LaCoO_3$ perovskite type oxide pulverized this a part of catalyst, and checked it by carrying out X diffraction measurement of this.
[0040][Catalytic activity evaluation] Next, toluene was oxidized on condition of the following (complete oxidation reaction to CO_2 and H_2O), the inversion rate of toluene at each temperature was measured, using as a catalyst the catalyst 1 acquired above, and the activity and performance of this catalyst were evaluated. Since a preliminary reaction is performed at 600 ** for 2 hours and catalytic activity was stabilized first, this activity examination was done by raising reaction temperature from low temperature gradually to an elevated temperature. Thus, the inversion rate of toluene at each measured predetermined reaction temperature is shown in Table 1.
[0041]reaction condition: -- reaction method: -- ordinary pressure flow method distributed gas presentation: -- toluene 500ppm -- 21% of; oxygen; nitrogen balance space-velocity (GHSV): -- 50,000h^{-1} reaction temperature: -- 200-350**;, however a preliminary reaction -- 600 ** (2h)
[0042]After dissolving acetic acid lantern hydrate (7.9 % of the weight of water content) 35 weight section in the mixed solvent of example 2 [catalyst preparation] 2-ethoxyethanol 700 weight section and triethanolamine 150 weight section, cobaltous acetate 4 hydrate 25 weight section was dissolved, it stirred well, and the impregnation solution was prepared.

[0043]Impregnate the honeycomb shape shaping carrier made from cordierite with this impregnation solution, and after that, at 150 **, dry for 5 hours and it ranks second, The carried catalyst (catalyst 2) of the request which carries out air calcination at 550 ** for 2 hours and by which formation support of the $LaCoO_3$ perovskite type oxide was carried out at 0.14g/cc of support rate on the field of this honeycomb carrier was acquired.
[0044]Formation of the $LaCoO_3$ perovskite type oxide pulverized this a part of catalyst,

and checked it by carrying out X diffraction measurement of this.
[0045][Catalytic activity evaluation] Next, the reduction reaction by ammonia of NO was performed on the following conditions, the inversion rate of NO at each temperature was measured, using as a catalyst the catalyst 2 acquired above, and the activity and performance of this catalyst were evaluated. Since a preliminary reaction is performed at 600 ** for 2 hours and catalytic activity was stabilized first, this activity examination was done by raising reaction temperature from low temperature gradually to an elevated temperature. Thus, the inversion rate of NO at each measured predetermined reaction temperature is shown in Table 2.
[0046]reaction condition: -- reaction method: -- ordinary pressure flow method distributed gas presentation: -- NO. 200ppm;$SO_2$100 -- 10% of ppm;$NH_3$200ppm; oxygen;H_2O 5%; nitrogen balance space-velocity (GHSV): -- 30,000h^{-1} reaction temperature: -- 300-400**;, however a preliminary reaction -- 600 ** (2h)
[0047]Example 3 [catalyst preparation] acetic acid lantern hydrate (7.9 % of the weight of water content) 35 weight section, It dissolved in the mixed solvent of 2-methoxyethanol 880 weight section and triethanolamine 340 weight section which prepared independently cobaltous acetate 4 hydrate 25 weight section and strontium acetate 22 weight section, respectively, and each solution was prepared. Next, the solution of each above was taken so that it might be set to mole-ratio La:Sr:Co=4:1:5, these were mixed, and it was considered as the impregnation solution.
[0048]Impregnate the honeycomb shape shaping carrier made from cordierite with this impregnation solution, and after that, at 150 **, dry for 5 hours and it ranks second, The carried catalyst (catalyst 3) of the request which carries out air calcination at 600 ** for 2 hours and by which formation support of the $La_{0.8}Sr_{0.2}CoO_3$ perovskite type oxide was carried out at 0.14g/cc of support rate on the field of this honeycomb carrier was acquired.
[0049]Formation of the $La_{0.8}Sr_{0.2}CoO_3$ perovskite type oxide pulverized this a part of catalyst, and checked it by carrying out X diffraction measurement of this.
[0050][Catalytic activity evaluation] The reduction reaction by ammonia of NO was performed on the same method and conditions as Example 2, using as a catalyst the catalyst 3 acquired above, and the activity was evaluated. This result is shown in Table 2.
[0051]After dissolving acetic acid lantern hydrate (7.9 % of the weight of water content) 35 weight section in the mixed solvent of example 4 [catalyst preparation] 2-methoxyethanol 600 weight section and diethanolamine 330 weight section, cupric-acetate anhydrate 9 weight section was dissolved, it stirred well, and the impregnation solution was prepared.
[0052]Impregnate the gamma-alumina carrier of a pellet type with this impregnation solution, and after that, at 150 **, dry for 5 hours and it ranks second, The carried catalyst (catalyst 4) of the request which carries out air calcination at 550 ** for 2 hours and by which formation support of the La_2CuO_4 perovskite similar type oxide was carried out at 0.15g/cc of support rate on the field of the gamma-alumina carrier of this pellet type was acquired.
[0053]Formation of the La_2CuO_4 perovskite similar type oxide pulverized this a part of catalyst, and checked it by carrying out X diffraction measurement of this.
[0054][Catalytic activity evaluation] Toluene was oxidized on the same method and conditions as Example 1, using as a catalyst the catalyst 4 acquired above, and the activity was evaluated. This result is shown in Table 1.
[0055]Comparative example 1 [catalyst preparation] lanthanum nitrate 6 hydrate 88 weight section and cobalt nitrate 6 hydrate 50 weight section were dissolved in pure water 500 weight section. It added in this solution gradually, stirring the solution which dissolved sodium hydroxide 61 weight section in pure water 500 weight section, and it was made to

generate precipitate. After filtration having recovered this precipitate and rinsing it, at 150 **, it dried for 5 hours, it ranked second, air calcination was carried out at 700 **, and the powdered $LaCoO_3$ perovskite type oxide was obtained.

[0056]Next, gamma-alumina 100 powdered weight section and pure water 100 weight section are added to this $LaCoO_3$ perovskite type oxide powder 10 weight section, After carrying out moisture control of the mixture obtained by mixing for 10 hours with the ball mill suitably, it was supported by the WOSHU coat method to the honeycomb shape shaping carrier made from cordierite (coating). Then, at 150 **, it dried for 5 hours, it ranked second, air calcination was carried out at 800 ** for 3 hours, and the solid content which consists of a $LaCoO_3$ perovskite type oxide and alumina on the field of this honeycomb carrier acquired the carried catalyst (catalyst R1) as a comparative example supported with the support rate which is 0.18g/cc.

[0057][Catalytic activity evaluation] Toluene was oxidized on the same method and conditions as Example 1, using as a catalyst the catalyst R1 acquired above, and the activity was evaluated. This result is shown in Table 1.

[0058]Comparative example 2 [catalyst preparation] lanthanum nitrate 6 hydrate 89 weight section and manganese nitrate 4 hydrate 35 weight section were dissolved in pure water 500 weight section. It added in this solution gradually, stirring the solution which dissolved sodium hydroxide 61 weight section in pure water 500 weight section, and it was made to generate precipitate. After filtration having recovered this precipitate and rinsing it, at 150 **, it dried for 5 hours, it ranked second, air calcination was carried out at 700 **, and the powdered $LaMnO_3$ perovskite type oxide was obtained.

[0059]Next, gamma-alumina 100 powdered weight section and pure water 100 weight section are added to this $LaMnO_3$ perovskite type oxide powder 10 weight section, After carrying out moisture control of the mixture obtained by mixing for 10 hours with the ball mill suitably, it was supported by the WOSHU coat method to the honeycomb shape shaping carrier made from cordierite (coating). Then, at 150 **, it dried for 5 hours, it ranked second, air calcination was carried out at 800 ** for 3 hours, and the solid content which consists of a $LaMnO_3$ perovskite type oxide and alumina on the field of this honeycomb carrier acquired the carried catalyst (catalyst R2) as a comparative example supported with the support rate which is 0.10g/cc.

[0060][Catalytic activity evaluation] The reduction reaction by ammonia of NO was performed on the same method and conditions as Example 2, using as a catalyst the catalyst R2 acquired above, and the activity was evaluated. This result is shown in Table 2.

[0061]

[Table 1]

触媒		転化率／%			
		200℃	250℃	300℃	350℃
実施例1	触媒1	82.0	98.2	100	100
実施例4	触媒4	80.2	97.8	100	100
比較例1	触媒R1	71.8	89.0	97.8	100

[0062]

[Table 2]

触媒		転化率／%		
		300℃	350℃	400℃
実施例2	触媒2	81.1	92.3	63.0
実施例3	触媒3	87.3	93.8	94.5
比較例2	触媒R2	71.0	85.6	78.8

[0063]Even if it changes the kind of carrier, and the kind of perovskite oxide so that clearly also from the result shown in Table 1 and 2, The direction of the support perovskite type oxide catalyst and support perovskite similar type oxide which were prepared by the method (how to use the support method of supporting the solution of said specific organic system mixed solvent as impregnating liquid) of this invention, The catalyst prepared by the method of supporting the method of using conventional solution as impregnating liquid and the particle obtained beforehand shows having the catalyst performance outstanding to oxidation reaction or a reduction reaction. This twists various kinds of perovskite oxides of a request on various kinds of carriers for formation support to be more effectively carried out to a high dispersion state (high surface area), when it prepares by the method of this invention.
Therefore, the catalyst performance superior to what is similarly depended on a conventional method to other various catalytic reaction (above) other than the reaction shown in the above-mentioned example is demonstrated.
It also checked that the performances (activity, endurance, etc.) various kinds of catalysts which added other catalyst components, such as the precious metals, by support etc. further actually excelled [performances] in various kinds of support perovskite oxide catalysts or this which was obtained by the method of this invention also to various kinds of reactions described above other than the above-mentioned reaction were shown.

[Translation done.]